

Annual Reports

VOLUME 72 1975 SECTION A
PHYSICAL AND INORGANIC CHEMISTRY

THE CHEMICAL SOCIETY

ISBN 0 85186 080 X
ISSN 0069-3022

Annual Reports
on the Progress of Chemistry
Volume 72, 1975

SECTION A
Physical and
Inorganic Chemistry

The Chemical Society
Burlington House, London W1V 0BN

Ref
540
C517A

V.72 SeA

ISBN: 0 85186 080 X

ISSN: 0069-3022

© Copyright 1976

by

The Chemical Society

Contributors

- P. W. Atkins, B.Sc., Ph.D., M.A., *University of Oxford*
R. P. Bell, M.A., F.R.S., *University of Stirling*
D. J. Cardin, B.Sc., D.Phil., *University of Dublin*
A. J. Carty, B.Sc., Ph.D., *University of Waterloo, Ontario, Canada*
R. H. Cragg, B.Sc., Ph.D., *University of Kent at Canterbury*
J. R. Dilworth, M.A., D.Phil., *University of Sussex*
K. R. Dixon, B.A., Ph.D., *University of Victoria, British Columbia, Canada*
M. Evans, B.Sc., Ph.D., *University of Oxford*
T. E. Faber, M.A., Ph.D., *University of Southampton*
T. P. Lambert, B.A., *University of Oxford*
M. F. Lappert, B.Sc., Ph.D., D.Sc., F.R.I.C., *University of Sussex*
G. J. Leigh, B.Sc., Ph.D., *University of Sussex*
G. R. Luckhurst, B.Sc., Ph.D., *University of Southampton*
R. L. Richards, B.Sc., Ph.D., *University of Sussex*
J. S. Rowlinson, M.A., D.Phil., F.R.I.C., F.I.Chem.E., F.R.S., *University of Oxford*
J. D. Smith, M.A., Ph.D., *University of Sussex*

Set in Times on Linotron Filmsetter and printed offset by
J. W. Arrowsmith Ltd., Bristol, England
Made in Great Britain

Preface

The recommendations of the 1975 Tertiary Publications Committee working party on *Annual Reports*, as outlined in the Preface to the 1974 Reports, have largely been successfully applied to the content of the 1975 Reports. The most apparent result of this is a further reduction in the length of both Sections: A, 244pp.; B, 472pp., but it is hoped that the general appeal of this long-established publication has also been enhanced. Any comments which readers may have on the content and approach of the present Reports would be welcomed by the Editorial staff as useful pointers to the most desirable format for future volumes.

The very marked reduction in length of the Physical Chemistry part of Section A, however, was not deliberate policy, and the low number of chapters is due to the fact that several of the contributions originally commissioned were not completed in time to be included in the 1975 Reports. Professor R. P. Bell, F.R.S., has now completed his term of office for this Part and we thank him for his efforts over the past three years in eliciting some very valuable contributions. We welcome Professor M. F. Lappert as Senior Reporter for the Inorganic Chemistry Part of Section A, and he has already made changes in the scope and depth of coverage of this area, as detailed in his Introduction to this Part.

Dr. M. F. Ansell and Professor P. G. Sammes have continued as Senior Reporters for Section B, Organic Chemistry, and we thank the former for carrying out his duties as far as possible during a period of illness, and the latter for shouldering the extra burdens thereby placed upon him. Again, the specific steps they have taken to meet the Society's length requirements are described in their Introduction to Section B.

Contents

Part I Physical Chemistry

| | | |
|-----------|--|----|
| Chapter 1 | Introduction | 3 |
| | <i>By R. P. Bell</i> | |
| Chapter 2 | The Motion of Simple Molecules in Liquids | 5 |
| | <i>By J. S. Rowlinson and M. Evans</i> | |
| 1 | Introduction | 5 |
| 2 | The Velocity Auto-correlation Function | 5 |
| 3 | The Density-Density Correlation Function | 11 |
| 4 | The Simulation and Measurement of Correlation Functions in Monatomic Liquids | 14 |
| 5 | Absorption in Molecular Liquids | 17 |
| 6 | Depolarized Rayleigh Scattering—a Study of $^{(R)}\psi(t)$ | 21 |
| 7 | N.M.R. Spin-Rotation Relaxation—a Study of $^{(I)}\psi(t)$ | 27 |
| Chapter 3 | Liquid Crystals | 31 |
| | <i>By G. R. Luckhurst and T. E. Faber</i> | |
| 1 | Introduction | 31 |

Part I Molecular Behaviour 32

| | | |
|---|----------------------------|----|
| 2 | Orientalional Order | 32 |
| | Nematics | 32 |
| | Cholesterics | 38 |
| | Smectic A | 39 |
| | Smectic C | 39 |
| 3 | Molecular Dynamics | 40 |
| | Translational Diffusion | 40 |
| | Rotation | 43 |

| | |
|---|-----------|
| Part II Continuum Behaviour | 47 |
| 4 Continuum Theory for Nematics and Cholesterics | 47 |
| Curvature Elasticity | 47 |
| Viscosity | 49 |
| 5 Applications of Continuum Theory | 51 |
| Freedericksz Transitions | 51 |
| Disclinations | 53 |
| Flow Alignment | 54 |
| Ultrasonic Attenuation | 55 |
| Surface Ripples | 56 |
| Rayleigh Scattering | 56 |
| Nuclear Magnetic Relaxation | 57 |
| 6 Dynamic Instabilities | 58 |
| Thermal Convection | 58 |
| Electrohydrodynamic Convection | 60 |
| Convection Induced by Shear Flow | 60 |
| 7 Smectics | 61 |
| Continuum Theory of the Smectic A Phase | 61 |
| Pre-Smectic Behaviour in Nematics | 62 |
| Dislocations and Flow in Smectics | 63 |
| Chapter 4 The Effect of a Magnetic Field on Chemical Reactions | 67 |
| <i>By P. W. Atkins and T. P. Lambert</i> | |
| 1 Historical Background | 67 |
| 2 The General Theoretical Background | 70 |
| 3 Experimental Examples | 74 |
| 4 Electrochemiluminescence | 78 |
| 5 Conclusion | 88 |
| Part II Inorganic Chemistry | |
| Chapter 5 Introduction | 91 |
| <i>By M. F. Lappert</i> | |
| Chapter 6 The Typical Elements | 93 |
| Part I: Groups I and II | 93 |
| <i>By R. H. Cragg</i> | |
| 1 Group I | 93 |
| 2 Group II | 95 |

Part II: Group III 95
By A. J. Carty

| | |
|--|-----|
| 1 Boron | 95 |
| Boron Hydrides and Borane Anions | 95 |
| Theoretical Studies of Bonding and Structure | 95 |
| Structures of Boranes | 97 |
| Synthesis and Structures of Borane Anions | 98 |
| Metalloboranes | 99 |
| Metal Complexes of the Tetrahydroborate Ion | 100 |
| Carbaboranes and Metallocarbaboranes | 101 |
| Intramolecular Rearrangements | 101 |
| Synthesis | 105 |
| Structures of Carbaboranes and Metallocarbaboranes | 106 |
| Boracarbocycles and Their Metal Complexes | 108 |
| Boron–Carbon π -Bonding in Vinylboranes | 110 |
| Boron Halides | 110 |
| The Boron–Phosphorus Bond | 111 |
| The Boron–Nitrogen Bond | 112 |
| Boron Carbides | 113 |
| 2 Aluminium, Gallium, Indium, and Thallium | 114 |
| Structure and Bonding in Aluminates | 114 |
| The Co-ordination Sphere of Aluminium in Solution | 115 |
| Aluminium–Halogen Compounds | 115 |
| Compounds with Aluminium–Hydrogen Bonds | 116 |
| Transition Metal–Gallium, –Indium, and –Thallium Bonds | 116 |
| Synthesis of Indium(III) and Indium(I) Compounds | 117 |
| Pentahalogenometallates(III) | 118 |
| Stereochemical Activity of the Thallium(I) Lone Pair | 118 |

Part III: Groups IV and V 119
By J. D. Smith

| | |
|---|-----|
| 1 Reactions of Hydrides | 119 |
| 2 Cage Compounds | 122 |
| 3 Polyatomic Anions | 123 |
| 4 Alkylamido-derivatives and Alkoxides | 124 |
| 5 Lone-pair Stereochemistry | 125 |
| 6 Trends in Bond Order | 126 |
| 7 Gas-phase Basicities | 127 |

| | |
|---|-----|
| 8 Diphosphines | 129 |
| 9 Methylidynephosphine | 130 |
| 10 Phosphinidene and Arsinidene Complexes | 130 |
| 11 Phosphazenes | 132 |
| 12 Reactions of Phosphorus Esters | 135 |
| Part IV: Groups VI—VIII | 137 |
| By R. H. Cragg | |
| 1 Group VI | 137 |
| 2 Group VII | 143 |
| 3 Group VIII | 146 |
| Chapter 7 Transition-metal Chemistry | 149 |
| By J. R. Dilworth, G. J. Leigh, and R. L. Richards | |
| 1 Groups IV and V: Titanium, Zirconium, and Hafnium; Vanadium, Niobium, and Tantalum | 149 |
| 2 Group VI: Chromium, Molybdenum, and Tungsten | 154 |
| Complexes with Metal–Metal bonds | 154 |
| Nitrogen Fixation and other Reactions of Biological Significance | 155 |
| 3 Group VII: Manganese, Technetium, and Rhenium | 159 |
| Manganese Porphyrin and Related Complexes | 159 |
| Complexes with Metal–Metal Multiple Bonds | 161 |
| 4 Group VIIIA: Iron, Ruthenium, and Osmium | 162 |
| Synthetic Dioxygen Carriers | 162 |
| Iron–Sulphur Cluster Systems | 164 |
| Ruthenium Ammine Complexes | 166 |
| 5 Group VIIIB: Cobalt, Rhodium and Iridium | 167 |
| Dioxygen as a Ligand | 167 |
| Chelate Complexes of Biological Relevance | 169 |
| Complexes of Sulphur Ligands | 170 |
| Chelating Phosphine Complexes | 171 |
| Reactions of Co-ordinated Ligands and Catalysis | 171 |
| 6 Group VIIC: Nickel, Palladium, and Platinum | 172 |
| Complexes of Multidentate Ligands | 172 |
| Zerovalent Complexes | 174 |
| Oxidation State One | 175 |
| Nuclear Magnetic Resonance Studies | 175 |
| Hydrocarbon Activation | 176 |
| Diazeno Ligands | 176 |

| | |
|---|-----|
| 7 Group IB: Copper, Silver, and Gold | 176 |
| Structural and Magnetic Studies | 176 |
| Unusual Valence States and Biologically Related Complexes | 177 |
| Chapter 8 Organometallic Compounds | 179 |
| <i>By D. J. Cardin and K. R. Dixon</i> | |
| 1 Introduction | 179 |
| 2 Reactions of Metal Atoms | 179 |
| 3 Carbene and Carbyne Complexes | 180 |
| 4 α and β-Eliminations | 182 |
| 5 Organo-lanthanides and -actinides | 183 |
| 6 Cyclopentadienyl and Cyclo-octatetraenyl Compounds | 183 |
| 7 Hydrometallations | 185 |
| 8 Sixteen-electron Compounds | 186 |
| 9 Silacyclopropanes | 186 |
| 10 Main-group Organometallic Ions | 188 |
| 11 Double-bonded Silicon | 188 |
| 12 Silatranes and Stannatranes | 189 |
| 13 Ylides | 190 |
| 14 Chiral Metal Centres | 191 |
| 15 Metal–Carbon Bond Strength Data | 192 |
| 16 Olefin Metathesis | 193 |
| 17 Metal–Metal Bonds and Clusters | 193 |
| 18 Shorter Topics | 195 |
| 19 Books and Reviews: Main-group and Early Transition Elements | 197 |
| 20 Metal Carbonyls | 198 |
| Matrix Isolation of Radical Species and other Metal Carbonyl Transients | 198 |
| Photochemistry | 199 |
| Fluxional Processes | 200 |
| Bridging Carbonyl Structures | 203 |
| Cluster Carbonyl Systems | 204 |
| Platinum(II) and Palladium (II) | 205 |
| 21 Metal Hydrides | 207 |

| | |
|---|---------|
| 22 Organometallic Compounds | 208 |
| One-carbon Ligands | 208 |
| Alkyls | 208 |
| Insertions Reactions | 209 |
| Oxidative Addition | 211 |
| Dialkylaminomethyl and Dialkylphosphinomethyl Ligands | 212 |
| Two-carbon Ligands | 212 |
| Aza-allyl Complexes and Related Species | 212 |
| Phosphonium Betaine Complexes | 214 |
| Trisethyleneplatinum and Related Species | 214 |
| Formation and Cleavage of C—C Bonds at Metal Sites | 215 |
| 23 Catalytic Processes | 218 |
| Author Index | 221 |

Section B, Organic Chemistry, contains the following items

- 1 Introduction. By M. F. Ansell and P. G. Sammes
- 2 Physical Methods and Techniques
 - Part (i) Mass Spectrometry. By T. P. Toubé
 - Part (ii) Nuclear Magnetic Resonance Spectroscopy. By L. Phillips
 - Part (iii) X-Ray Crystallography. By M. B. Hursthouse and S. Neidle
 - Part (iv) Infrared and Raman Spectroscopy. By G. A. Newman
- 3 Theoretical Chemistry. By G. Klopman
- 4 Reaction Mechanisms
 - Part (i) Orbital Symmetry Correlations and Pericyclic Reactions.
By D. W. Jones
 - Part (ii) Polar Reactions. By T. W. Bentley
 - Part (iii) Electron Spin Resonance and Free Radical Reactions.
By A. T. Bullock
- 5 Arynes, Carbenes, Nitrenes, and Related Species. By R. C. Storrs
- 6 Organometallic Chemistry
 - Part (i) Transition Elements. By R. Pearce, D. J. Thompson, and
M. V. Twigg
 - Part (ii) Main-group Elements. By K. Smith
- 7 Electro-organic Chemistry. By J. H. P. Utley
- 8 Photochemistry. By W. M. Horspool
- 9 Aliphatic Compounds
 - Part (i) Hydrocarbons. By D. Taylor
 - Part (ii) Other Aliphatic Compounds. By E. W. Colvin
- 10 Aromatic Compounds. By R. G. Coombes
- 11 Heterocyclic Chemistry. By O. Meth-Cohn and R. K. Smalley
- 12 Alicyclic Chemistry. By A. Cox
- 13 Synthetic Methods. By G. Pattenden
- 14 Biological Chemistry
 - Part (i) Insect Chemistry. By R. Baker and D. Evans
 - Part (ii) Steroids. By D. N. Kirk
 - Part (iii) Enzyme Mechanisms. By A. D. B. Malcolm and J. R. Coggins
 - Part (iv) Nucleic Acids. By R. J. H. Davies
 - Part (v) Biosynthesis. By R. B. Boar and D. A. Widdowson

PART I
PHYSICAL CHEMISTRY

1 Introduction

By R. P. BELL

Department of Chemistry, University of Stirling, Stirling FK9 4LA

Owing to circumstances outside the control of the Senior Reporter, this year's section on physical chemistry is regrettably brief. In addition to the three articles which follow it was planned to include reviews on Raman spectroscopy and on thermal explosions, but both of these failed to materialise, though it is hoped that the former may be included in next year's *Annual Reports*. As a result the scope of this year's reports is narrower than usual, though this is in keeping with the general policy followed during the past few years of commissioning critical essays on particular topics rather than attempting to cover wider fields of physical chemistry. Contributors have again been asked to restrict themselves to about 100 key references in each article, and it is hoped that this contributes to the readability of the product.

The first chapter deals with molecular motion in simple liquids, and in particular with its interpretation in terms of correlation functions. This approach will be unfamiliar to many chemists, but its introduction has led to a striking unification of our ideas about a wide range of time-dependent phenomena. (In this respect its influence might be compared with that of group theory in clarifying problems of molecular symmetry). As a result a variety of transport and scattering phenomena can be used to obtain information about the detailed motion executed by molecules in simple liquids, which is fundamental to our understanding of their physical properties and of the mechanism of chemical reactions in the liquid phase.

The second article is on liquid crystals, which constitute a special state of matter intermediate between crystals and amorphous liquids. They are formed only by restricted classes of rather complex organic compounds and although their existence has been known since 1888 they were for many years regarded as a chemical curiosity. Recently, however, much progress has been made towards a quantitative understanding of such systems, partly by experimental techniques such as light-scattering, n.m.r. spectroscopy and dielectric relaxation, and partly by theoretical developments. The present report concentrates on the latter, and shows that both molecular pictures and continuum dynamics can make useful contributions to the problem. It is worth noting that liquid crystals are now used extensively as solvents in spectroscopy and in electro-optic display devices, though these topics are not included in the present review.

The final section reviews the effects of external magnetic fields on chemical reactions. Although the existence of such effects has been repeatedly claimed (and denied) for many years, it seems likely that most of the early work in this field is both experimentally and theoretically unsound. Recently, however, a clear understanding has been reached of the conditions under which appreciable effects may be expected, and there is ample experimental evidence to support the theoretical conclusions. As might be expected, this relates to processes involving a change of

multiplicity, and substantial effects have been observed both in the rates of chemical reactions and in fluorescence. The authors conclude by pointing out that there is ample scope for further experimental work in this field, and that magnetic effects on radical reactions may well have industrial significance.

2 The Motion of Simple Molecules in Liquids

By J. S. ROWLINSON and M. EVANS

Physical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ

1 Introduction

In a dilute gas the molecules move freely with a spread of velocities given by the Maxwell-Boltzmann distribution. After they have moved for distances many times their diameters they collide with other molecules and are deflected into new rectilinear paths. Their mean motion over a long time is measured by the coefficient of diffusion, which can be expressed in terms of the angles of deflection of the colliding pairs.¹

In liquids matters are not so simple since each molecule is in perpetual interaction with its neighbours; there are no mean-free-paths and no binary collisions. Molecules can also rotate in an irregular manner about one or more axes under the influence of the torques exerted by their neighbours or by an external field. The molecular motions can be studied on a macroscopic scale by measuring, for example, rates of diffusion or dielectric relaxation, but the relation of these crude macroscopic averages to what is happening at a molecular level is a difficult task. The purpose of this review is to describe the progress that has been made in this field in the past ten years.

Sections 2 and 3 introduce the statistical language used to describe molecular motion, the language of correlation functions and their spectra, or Fourier transforms. Perhaps the greatest advance of the past ten years has been the systematic use of this language to describe ever-increasing regions of chemical physics: statistical mechanics, the scattering of light, X-rays and neutrons, i.r., Raman and n.m.r. spectroscopy are subjects which have gained in precision and unity from these developments. Section 4 describes the measurement and computer simulation of the correlation functions of a monatomic liquid. Sections 5—7 extend the discussion to simple molecular liquids with emphasis on the study of orientational correlation functions by far-i.r. spectroscopy and light scattering. We give no derivations or proofs, only statements and references.

2 The Velocity Auto-correlation Function

A *distribution function* is an answer to a question of the following form: if there is a molecule with a specified position, orientation, velocity *etc.* at a certain time $t = 0$, what is the probability that there will be a molecule (the same or different) at a position distant by r , with an orientation changed by ϕ , with a velocity increased by v

¹ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, 'Molecular Theory of Gases and Liquids', Wiley, New York, 1954.

etc., at a time t ? Such a function can be very complicated but often we are not interested in all these variables. Thus the equilibrium or thermodynamic properties are described by a time-averaged distribution function, or, what is equivalent, by an average taken over an ensemble of systems at a fixed time $t = 0$. They are functions of \mathbf{r} and ϕ alone or, in a monatomic fluid, of \mathbf{r} alone.² The dynamic and transport properties in which we are here interested can be described only if we know the time evolution of these functions, but then we can often ignore one of the other variables, *e.g.* \mathbf{r} or ϕ .

The term *correlation function* (which we abbreviate *c.f.*) is used to describe a distribution function which has been normalized so as to approach zero for large values of the argument r and/or t (as is appropriate). It describes the degree of correlation between two events; such correlation is zero at large times or distances in an isotropic fluid. The most familiar distribution function is probably the radial function $g(r)$, which describes the equilibrium probability of there being two molecules at a separation r , and which can be measured from the X-ray diffraction pattern. At large separations this approaches unity (see below, Section 3), and the corresponding *c.f.* is therefore $g(r) - 1$, which is usually called $h(r)$, the total correlation function. We consider below (Section 3) the generalization of $h(r)$ to include time-dependence but start first with a more simple one-molecule *c.f.*, the velocity auto-correlation function.

If a molecule has a velocity $\mathbf{v}(0)$ at $t = 0$, and a velocity $\mathbf{v}(t)$ at time t then a suitable measure of the degree of correlation of these velocities is the scalar product $\mathbf{v}(0) \cdot \mathbf{v}(t)$. After a sufficiently long time, *e.g.* 10^{-10} s, the magnitude and direction of $\mathbf{v}(t)$ will bear no relation to that of $\mathbf{v}(0)$ and so the scalar product goes to zero. The velocity auto-correlation function is defined as the average of this product over all molecules in a system at equilibrium, and is denoted $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$. It is convenient to use the symbol $\psi(t)$ for the normalized function $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle / \langle \mathbf{v}(0)^2 \rangle$. The importance of this function is its close relation to the coefficient of diffusion, but before discussing this it is useful to examine the behaviour of correlation functions in general, and this one in particular, as functions of time.

Consider first an almost collision-free gas in which a molecule has the same velocity at t as it has at $t = 0$. Hence the *c.f.* $\psi(t)$ is a constant, namely unity, since

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle = \langle \mathbf{v}(0)^2 \rangle = 3kT/m \quad (1)$$

where m is the mass of the molecule. A second idealized case is the perfect Einstein solid in which a molecule vibrates about a site at a constant angular frequency ω_E ; here the *c.f.* is an oscillatory function proportional to $\cos(\omega_E t)$. A liquid behaves in an intermediate fashion as is shown in Figure 1, which is based on a computer simulation discussed in Section 4. The *c.f.* is constant or gas-like at short times (typically $t < 10^{-13}$ s), it oscillates weakly, and goes to zero at long times. The first negative region is easily explained as the rebound as a molecule reverses its velocity on colliding with a neighbour after travelling on average for the mean molecular separation.

² (a) H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, 'Physics of Simple Liquids', North-Holland, Amsterdam, 1968; (b) C. A. Croxton, 'Liquid State Physics', Cambridge University Press, 1974; (c) A. F. M. Barton, 'The Dynamic Liquid State', Longmans, London, 1974.

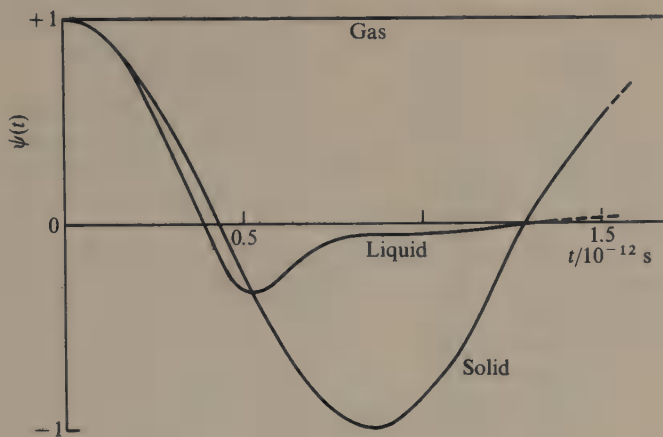


Figure 1 The normalized velocity auto-correlation function for a collision-free gas, for an Einstein solid and for a liquid. The last is based on results obtained by computer simulation discussed in Section 4

Each c.f. has a Fourier transform, and if the variable of the c.f. is time, as here, then that of the transform is frequency. We define the transform of $\psi(t)$ by

$$\tilde{\psi}(\omega) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \psi(t) e^{-i\omega t} dt \quad (2)$$

and, conversely, we have also the important relation

$$\psi(t) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \tilde{\psi}(\omega) e^{i\omega t} d\omega \quad (3)$$

The function $\tilde{\psi}(\omega)$ is called the spectrum of $\psi(t)$ since it can be regarded as the 'sampling' of $\psi(t)$ by a signal of frequency ω . It is often easier to measure the spectra than the functions themselves. Equations (2) and (3) show that we can pass freely from c.f. to its spectrum, and *vice versa*, providing we know one of them for all values of its argument. In practice this is a considerable restriction.

The spectra of the three cases considered above can be found at once. If $\psi(t)$ is unity, then $\tilde{\psi}(\omega)$ is zero unless $\omega = 0$, and is infinite if $\omega = 0$. That is,

$$\tilde{\psi}(\omega) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} e^{-i\omega t} dt = (2\pi)^{\frac{1}{2}} \delta(\omega) \quad (4)$$

where $\delta(\omega)$ is Dirac's delta function. This is zero everywhere except where its argument is zero, where it is infinite, and it is normalized to unity,

$$\int_{-\infty}^{\infty} f(x) \delta(x - x^*) dx = f(x^*) \quad \int_{-\infty}^{\infty} \delta(x) dx = 1 \quad (5)$$

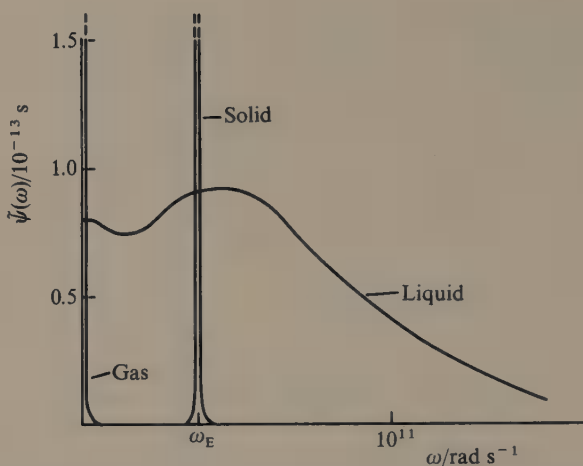


Figure 2 *The Fourier transforms of the correlation functions of Figure 1. Those for gas and solid are delta-functions, whilst that for the liquid has two broad components, a diffusive mode centred on $\omega = 0$, and an oscillatory mode at frequencies comparable with ω_E of the solid*

Thus the spectrum of a collision-free gas is a sharp line at zero-frequency; it will be seen below that the diffusion coefficient is then infinite. For an Einstein solid the c.f. is obtained by integrating the product of $e^{-i\omega t}$ and $\cos(\omega_E t)$, and this integral is zero unless $\omega = \omega_E$, so that the spectrum is now a sharp line at the Einstein frequency, or $\psi(\omega)$ is proportional to $\delta(\omega - \omega_E)$. For a liquid we have again both features in the spectrum. The integration of the curve in Figure 1 produces a spectrum with two peaks, characteristic of diffusional and oscillatory motion, but both are now very broad (Figure 2).

Thus the c.f. and its spectrum enable us to describe succinctly the essential features of translational motion in a liquid more accurately than was possible with the 'models' of the liquid state that used to be so popular; in which diffusion, for example, might be treated as an activated jump from one site to another. However, if we are to use these correlation functions we must be able to observe them or their spectra, to relate them on the one hand to macroscopic properties such as diffusion coefficients, and on the other to intermolecular forces by the methods of statistical mechanics. In the rest of this section we say something of the second of these problems, and touch on the fringes of the third. The first, the measurement of correlation functions, we cover in Section 4.

The connection between correlation functions and macroscopic properties is a consequence of two broad and related generalizations which lie at the root of our present understanding of transport properties. These are linear response theory and a theorem linking dissipative processes and the regression of fluctuations. Neither is new, for specialized versions of both were used for many years by Einstein, Onsager, and others, but the realization of their power and generality is much more recent; it

stems from the work of Callen, Green, Kubo, and others³⁻⁶ during the years 1955-1965. Linear response theory describes the behaviour of two weakly coupled systems, as for example, when a beam of light or neutrons interacts with, and is scattered by a liquid, or when a beam of sound is absorbed and dispersed. Because the coupling is weak it follows that the response of the liquid can be calculated from a knowledge of its behaviour in the absence of the stimulus. This behaviour is described in terms of correlation functions of the appropriate dynamical variables (velocities, energies, *etc.*) in which the averages denoted by angle brackets are, it is important to note, averages over a system at equilibrium. By suitable ingenuity (sometimes called 'indirect Kubo methods') the stimulus can be chosen so that the response can include diffusional or viscous motion, or transport of thermal energy,^{3,4} and so we are able to relate these transport, or non-thermodynamic, properties to averages over systems at equilibrium.

The theorem on fluctuations stems from a hypothesis due to Onsager which lies behind his reciprocal relations between coupled transport processes. Every system at equilibrium exhibits small departures from the average values of unconstrained dynamical properties (*e.g.* fluctuations of energy in a system at fixed temperature). These fluctuations regress with time and Onsager's result is that the average rate of their regression is governed by the usual macroscopic transport coefficients (*e.g.* thermal conductivity for thermal energy).⁷ Again, we have this direct relation between a transport or dissipation process and a purely equilibrium phenomenon, *viz.* fluctuations.

These theorems lead to simple relations between the transport properties and the correlation functions, relations which can now be derived in at least six different ways of different assumptions and rigour,³ and about whose truth there can now be no doubt. The first relation, due originally to Einstein, is the one most directly connected with the subject of this review for it shows that the coefficient of diffusion is the time-average of the velocity c.f.

$$D = \int_0^{\infty} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt \quad (6)$$

or, from equation (3)

$$D = \frac{3kT}{2m} (2\pi)^{\frac{1}{2}} \tilde{\psi}(0) \quad (7)$$

It is characteristic of hydrodynamic properties such as diffusion and viscosity, that they are related to the zero-frequency intercept (Figure 2) of $\tilde{\psi}$ and similar functions. In fact the spectrum of a time-dependent c.f. can be regarded as a frequency-dependent transport coefficient. More recent results relate other transport coefficients^{3,8} to integrals over other correlation functions.

³ R. Zwanzig, *Ann. Rev. Phys. Chem.*, 1965, **16**, 67.

⁴ R. Kubo, *Reports Progr. Phys.*, 1966, **29**, 255.

⁵ W. Marshall and S. W. Lovesey, 'Theory of Thermal Neutron Scattering', Clarendon Press, Oxford, 1971, Chap. 11 and Appendix B.

⁶ H. Mori, *Progr. Theor. Phys.*, 1965, **33**, 423; P. Schofield, in 'Statistical Mechanics', ed. K. Singer, (Specialist Periodical Reports), The Chemical Society, London, Vol. 2, 1975.

⁷ H. C. Longuet-Higgins, *Mol. Phys.*, 1963, **6**, 65.

⁸ P. A. Egelstaff, *Reports Progr. Phys.*, 1966, **29**, 333.

The second problem, the relation of a c.f. to the underlying molecular behaviour, is more difficult and largely unsolved. One useful route which has been much followed recently is to express the c.f. in terms of so-called *memory functions*, which are believed to have more simple structures. This idea has a lot in common with the reduction of the total (static) correlation function $h(r)$ by expressing it in terms of the apparently more simple direct correlation function $c(r)$ of Ornstein and Zernike.^{9,10} This reduction, which was re-introduced into modern statistical mechanics by Rushbrooke and Scoins,¹¹ has proved to be particularly fruitful, for it is easier to make intelligent approximations for $c(r)$ than for $h(r)$; for example, the Percus-Yevick approximation which lies behind much recent work on the static structure of liquids.^{2,10} The introduction of memory functions into the time-dependent correlation functions is leading to equally fruitful approximations.

This approach is best described by discussing first the problem of Brownian motion, or the diffusion of a particle of essentially infinite mass m . Its motion may be described by Langevin's equation⁶

$$m\dot{\mathbf{v}}(t) = -m\mathbf{c}\mathbf{v} + \mathbf{K}(t) \quad (8)$$

which separates the total force into two parts, a frictional retardation proportional to the velocity (c is a constant), and a randomly fluctuating force $\mathbf{K}(t)$ which arises from the impacts of the molecules of the liquid in which the particle is suspended. The two forces are not unrelated for interaction with the molecules of the liquid is also the cause of the frictional retardation. This relation between the random and the systematic components is a very general phenomenon and when put into precise form becomes the mathematical expression of the fluctuation-dissipation theorem.⁴

Since the molecules hitting the Brownian particle are light, and their impacts frequent and (almost) independent, it is usual to assume that $\mathbf{K}(t)$ is a Gaussian process with a correlation time negligibly short compared with the time steps of the Brownian motion. That is

$$\langle \mathbf{K}(0) \cdot \mathbf{K}(t) \rangle \propto \delta(t) \quad (9)$$

It follows^{3,4,6} that the velocity c.f. of the Brownian particle is an exponential in the magnitude of the time:

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle = \langle v^2 \rangle \exp(-c|t|) \quad (10)$$

and

$$D = kT/mc \quad (11)$$

where c is the constant in equation (8). Such exponential decay is a valid solution for a massive particle but it will not do if the particle is itself one of the molecules of the liquid. The results in Figure 1 show that $\psi(t)$ is more complicated than (10), and, moreover, it is an even function of time whose derivative vanishes at $t=0$, for at infinitesimally short times $v(t)$ must be the same as $v(0)$. Langevin's equation has

⁹ L. S. Ornstein and F. Zernike, *Proc. Acad. Sci. Amsterdam*, 1914, **17**, 793, reprinted in 'Equilibrium Theory of Classical Fluids', ed. H. L. Frisch and J. L. Lebowitz, Benjamin, New York, 1964.

¹⁰ A. Münster, 'Statistical Thermodynamics', Springer-Verlag, Berlin, 1969, Vol. 1, Chap. 10.

¹¹ G. S. Rushbrooke and H. I. Scoins, *Proc. Roy. Soc.*, 1953, **A216**, 203.

therefore been generalized for the discussion of molecular motion by the replacement of the constant c by what is, in effect, a frequency-dependent coefficient of friction. We write

$$m\dot{\mathbf{v}}(t) = -m \int_0^t \mathbf{v}(t-t')M_0(t') dt' + \mathbf{K}(t) \quad (12)$$

where $M_0(t)$ is a memory function which describes the past history of the friction, which is itself a correlation function, and which therefore has, in turn, a memory function which describes its own evolution.⁶ That is, there exists a function $M_1(t)$ defined by

$$\dot{M}_0(t) = - \int_0^t M_0(t-t')M_1(t') dt' \quad (13)$$

This argument can be extended indefinitely to $M_2(t)$, $M_3(t)$ etc. If we take the correlation of (12), (13), etc. with $\mathbf{v}(0)$, use the fact that this velocity is not correlated with $\mathbf{K}(t)$,

$$\langle \mathbf{v}(0) \cdot \mathbf{K}(t) \rangle = 0 \quad (14)$$

and take Laplace transforms* of each expression, then Mori showed that we obtain the transform $\tilde{\psi}(p)$ of the original c.f. $\psi(t)$ as a continued fraction.⁶

This approach is useful only if the memory functions are more simple than the original c.f. The first $M_0(t)$ will show a peak at $t=0$, representing the quasi-Brownian or inertial motion of the molecule, and a tail at longer times representing the damped oscillatory motion. (The memory function of an oscillator of frequency ω_E is a constant, ω_E^2 .) One might hope that, if not the first, then one of the low-order memory functions could be adequately approximated by a $\delta(t)$, thus truncating the continued fraction of Mori. In Section 4 we discuss the computer simulation of the velocity c.f. and in Section 5 extend the discussion to the rotational velocity c.f. and its memory functions, but first introduce, in the next section, a more general two-particle c.f.

3 The Density-Density Correlation Function

The velocity c.f. of the last section describes the motion of one molecule. It is equally important to be able to discuss the motions of pairs for two reasons; first, the intermolecular forces in a liquid are, to a first approximation, the sum of the interactions of the molecules in pairs only, and so we must know the static c.f. for pairs even to obtain the thermodynamic properties of internal energy, pressure etc., and, secondly, because the observed scattering of electromagnetic radiation by matter is a coherent interference of the scattering from two different centres.

Let the limiting[†] density on a molecular scale at point $\mathbf{r} = 0$ and at $t = 0$ be denoted

* A Laplace transform differs from a Fourier transform by the replacement of the oscillating function $\exp(-i\omega t)$ by the monotonically decaying function $\exp(-pt)$, so that $\tilde{\psi}(p)$ can be regarded as the result of sampling $\psi(t)$ by a probe with a relaxation time of p^{-1} . The integration in a Laplace transform is over all $t > 0$.

† The limit is the ratio $(\delta N / \delta V)$ of the number of molecules δN with centres in a volume δV containing the point $\mathbf{r} = 0$, as δV goes to zero.

$n(0, 0)$, and that at \mathbf{r} and t by $n(\mathbf{r}, t)$. We define a density-density distribution function $g^*(\mathbf{r}, t)$ by

$$g^*(\mathbf{r}, t) = n^{-1} \langle n(0, 0) n(\mathbf{r}, t) \rangle \quad (15)$$

where n is the mean number density, or N/V . If we average over an ensemble at a fixed time, say $t = 0$, then we obtain the static or, as it is commonly called, the radial distribution^{1,2} $g(\mathbf{r})$

$$ng(\mathbf{r}) = n^{-1} \langle n(0) n(\mathbf{r}) \rangle \quad (\mathbf{r} \neq 0) \quad (16)$$

We have, however, specified that there is a molecule at $\mathbf{r} = 0$, and so we have there a density described by the delta-function $\delta(\mathbf{r})$, and we have shown in (16) that the probability that there is a second molecule at \mathbf{r} is proportional to $ng(\mathbf{r})$. Hence

$$g^*(\mathbf{r}, 0) = \delta(\mathbf{r}) + ng(\mathbf{r}) \quad (17)$$

The two terms are called the *self* and the *distinct* parts of g^* . As time passes the first broadens out into a curve as the molecule originally at $\mathbf{r} = 0$ diffuses away, and this curve finally collapses to a line $g_{\text{self}}^* = 0$. The second term also loses its structures with time and goes finally to the constant value $g(\mathbf{r}) = 1$, (Figure 3). We therefore form the c.f. corresponding to g^* by subtracting this long-time limit and the result $G(\mathbf{r}, t)$ is called the van Hove c.f.¹²

$$G(\mathbf{r}, t) = g^*(\mathbf{r}, t) - n \quad (18)$$

The Fourier transform of this c.f. over the three dimensions of space and one of time is $S(\mathbf{k}, \omega)$, the *structure factor*,

$$S(\mathbf{k}, \omega) = \frac{1}{(2\pi)^2} \int_V \int_{-\infty}^{\infty} G(\mathbf{r}, t) \exp[i(\mathbf{r} \cdot \mathbf{k} - \omega t)] d\mathbf{r} dt \quad (19)$$

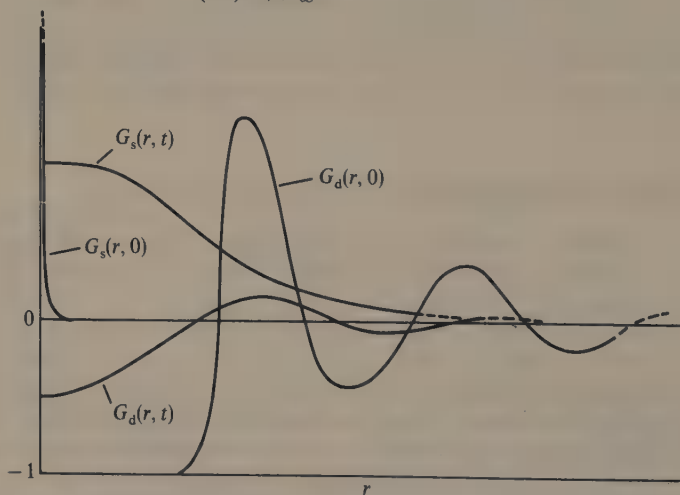


Figure 3 The self and distinct parts of van Hove's correlation function $G(\mathbf{r}, t)$. At zero time the self part is a delta-function at $\mathbf{r} = 0$ and the distinct is the (static) pair c.f. $h(\mathbf{r}) = g(\mathbf{r}) - 1$. At infinite time both parts go to zero

¹² L. van Hove, *Phys. Rev.*, 1954, **95**, 249.

It is the structure factor which is measured by the radiation (electromagnetic or neutron) scattered by the liquid. An incoming wave of length λ is characterized by a vector \mathbf{k}_0 which has the direction of the wave and a magnitude of $2\pi/\lambda$. The wave scattered with vector \mathbf{k}_1 has an intensity which is proportional to $S(\mathbf{k}, \omega)$, where $\mathbf{k} = \mathbf{k}_0 - \mathbf{k}_1$ and ω is the change of angular frequency. Alternatively, we can say that this wave has suffered a change of momentum of $\hbar\mathbf{k}$ and of energy $\hbar\omega$.

Neutrons scattered from a monoenergetic (or monochromatic) beam can be analysed for change of angle and speed, and so $S(\mathbf{k}, \omega)$ can be measured as a function of both variables, at least over limited ranges. The scattering can be either incoherent (from one centre) or coherent (from a pair of centres), according to the nature of the nucleus. Different isotopes of one atom behave differently in this respect. The former arises from the self-part of the c.f. and the latter from the distinct, and so, in particularly favourable cases, both parts of the transforms of G can be studied experimentally. Thermal neutrons have a wavelength of *ca.* 1 \AA and so k^{-1} is comparable with the intermolecular spacing, and the coherently scattered beam yields useful information on $G_{\text{distinct}}(\mathbf{r}, t)$ on taking the inverse transform.^{5,13}

If the analysis by speed (or energy) is omitted then what is obtained is an integral of $S(\mathbf{k}, \omega)$ over all ω , which is therefore a function of \mathbf{k} only, $S(\mathbf{k})$. Information on the time dependence of the c.f. has now been lost, and the transform of $S(\mathbf{k})$ yields only the static distribution function $g(r)$. With a beam of X-rays all the scattering is coherent, analysis by energy is virtually impossible and so only $S(\mathbf{k})$ and $g(r)$ can be observed. Neutron scattering has therefore told us about the dynamics of liquids in a way which was not possible with X-rays.

Visible light is scattered coherently with negligible change of momentum, and the spectrum observed is therefore $S(0, \omega)$. The change of frequency is small but observable if the incident light is from a laser and so highly monochromatic. Measurement of the intensity and angle but not the spectrum of the scattered light tells us only about the static properties. In particular $S(\mathbf{k} \approx 0)$ is related to the compressibility^{1,2,10}

$$(2\pi)^3 S(\mathbf{k} \approx 0) = n \int_v [g(r) - 1] dt = kT \left(\frac{\partial n}{\partial P} \right)_T - 1 \quad (20)$$

Such scattering is small in a normal liquid but intense near the critical point where $(\partial n / \partial P)_T$ is infinite.

The spectrum of the scattered light is more useful for it has three distinct peaks,¹⁴ a Rayleigh line at $\omega = 0$ and two Brillouin lines at $\omega = \pm Ws_w$, where W is the speed of sound in the liquid and s_w the wavenumber of the particular sound wave responsible for the scattering. The Rayleigh line arises from density (or more properly, refractive index) fluctuations arising from fluctuations of local entropy at fixed pressure. Such fluctuations do not propagate through the fluid and so the Rayleigh line is centred on $\omega = 0$. It may also contain a weak and very broad depolarized component, discussed in Section 6. The Brillouin lines arise from fluctuations of density due to fluctuations of pressure at fixed entropy. Such fluctuations propagate as sound waves which are

¹³ J. G. Powles, in 'Chemical Applications of Thermal Neutron Scattering', ed. B. T. M. Willis, Clarendon Press, Oxford, 1973.

¹⁴ D. McIntyre and J. V. Sengers, in ref. 2(a); H. L. Strauss, in 'Chemical Applications of Lasers', ed. C. B. Moore, Academic Press, New York, 1974.

present in all liquids at equilibrium, and which diffract the light at the appropriate Bragg angle. The frequency shift is a Doppler effect of the moving 'grating', and since the sound wave of appropriate length and orientation can be moving in either direction, a pair of lines is produced, one on each side of the incident frequency.

The Rayleigh and Brillouin lines provide a wealth of information, even for a monatomic liquid. The total intensity yields the compressibility (20), the ratio of intensities yield C_p/C_v , the width of the Rayleigh line yields the thermal diffusivity, and the displacement and width of the Brillouin lines yield the speed and coefficient of absorption of sound at frequencies above 10^{10} Hz, that is, above the range accessible by mechanically generated sound waves.¹⁵

4 The Simulation and Measurement of Correlation Functions in Monatomic Liquids

The study of the dynamics of liquids by computer simulation started with the work of Alder and Wainwright¹⁶ in 1959, who solved Newton's equations of motion for 32 hard spheres moving in a cubical box. It has progressed rapidly, hand-in-hand with the advances in computer speed and capacity, but even now it is clearly impossible to handle systems of 10^{23} molecules; the present practicable limit is about 10^3 , or perhaps up to 10^4 for particularly simple systems. In a sample of liquid of this size many molecules would be near a wall and so not representative of those in a bulk liquid. This problem is solved by surrounding the cubical sample on all sides by replicas of itself so that even molecules at a side or edge interact only with molecules in a similar environment.¹⁷ In these conditions even a sample of 1000 molecules is amply large enough to study the dynamics and thermodynamics of a liquid, since correlation functions decay virtually to zero over lengths of the order of 10 molecular diameters, except for liquids near their critical points.

Before we can solve the equations of motion we must choose an intermolecular potential, and the most popular for simulating the liquefied inert gases has been the Lennard-Jones (12, 6) potential,¹ which is a reasonable compromise between simplicity and realism. Geometrically more complicated potentials are now being used to simulate diatomic molecules;¹⁸ one of the most complicated that has so far been used is that chosen by Rahman and Stillinger¹⁹ for a simulation of water.

The first, and still perhaps the most informative simulation of the properties of a monatomic liquid was Rahman's study²⁰ of 864 Lennard-Jones (12, 6) particles confined to a cubic cell of side 10.2σ at a reduced temperature of $kT/\epsilon = 0.786$, where σ and ϵ are the collision diameter and depth of the Lennard-Jones potential. The density and temperature were chosen to simulate argon at 1.374 g cm^{-3} and 94.4 K. The velocity c.f. and its transform are shown in Figures 1 and 2. From the area under the curve in Figure 1 or, equivalently, from the intercept at zero frequency in Figure 2 we get a diffusion coefficient of $2.43 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$, which is the

¹⁵ D. Sette in ref. 2(a).

¹⁶ B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 1959, **31**, 459.

¹⁷ B. J. Alder and W. G. Hoover, and W. W. Wood, in ref. 2(a).

¹⁸ J. Barojas, D. Levesque, and B. Quentrec, *Phys. Rev.*, 1973, **A7**, 1092; P. S. Y. Cheung and J. G. Powles, *Mol. Phys.*, 1975, **30**, 921.

¹⁹ A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, 1971, **55**, 3336.

²⁰ A. Rahman, *Phys. Rev.*, 1964, **136**, A405.

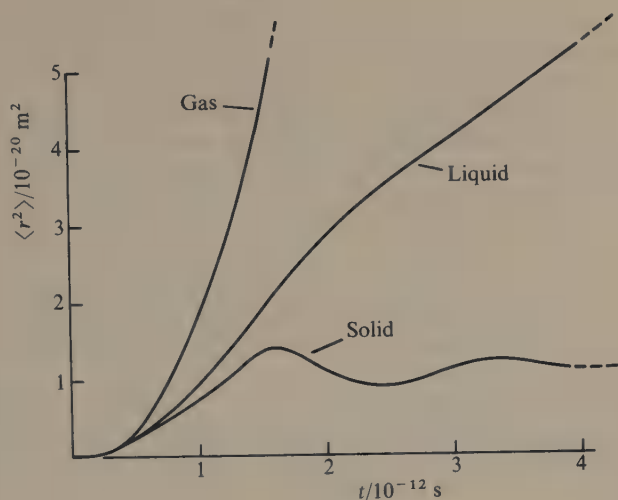


Figure 1 The mean-square displacement as a function of time (schematic)

same as that of liquid argon²¹ at a temperature of 90 K. However, the full curves give much more detailed information on the molecular motion than the value of the macroscopic or hydrodynamic coefficient of diffusion, and, in particular, show the inadequacy of the unmodified Langevin equation.

It is instructive to calculate the mean-square displacement, $\langle r^2 \rangle$, of any one molecule as a function of time (Figure 4). This was computed directly by Rahman, or, in principle, could have been obtained from the self-term of van Hove's c.f.

$$\langle r^2(t) \rangle = \int_0^\infty r^2 G_s(r, t) dr \quad (21)$$

At short time $\langle r^2 \rangle$ grows quadratically with time; that is, the motion of the molecule is unretarded, as in a perfect gas. For a crystal, in which the average is taken, from a fixed zero time, over the unrelated phases of the oscillators, $\langle r^2 \rangle$ settles down to a constant value. For a liquid the initially unretarded motion quickly passes into a linear dependence of $\langle r^2 \rangle$ on time, which corresponds to a constant rate of diffusion. For 'argon' this linear or hydrodynamic regime is reached after *ca.* $2.5 \times 10^{-12} \text{ s}$, a time in which a molecule has moved, on average, through a distance of about σ . The hydrodynamic regime is thus reached surprisingly quickly.

At high temperatures, or at densities substantially lower than those of a typical liquid, the negative region of the velocity c.f. disappears, and there is a monotonic fall with this increasing time. In this region the dissection of the c.f. into memory functions has proved useful.²² Much recent interest has centred about this decay to zero at long times of this positive c.f. in a fluid of moderate density. The decay is slow

²¹ J. Naghizadeh and S. A. Rice, *J. Chem. Phys.*, 1962, **36**, 2710.

²² D. Levesque and L. Verlet, *Phys. Rev.*, 1970, **A2**, 2514.

(i.e., not exponential) and the consensus of opinion²³ is that at long times it goes as t^{-3} . Such a slow decay gives rise to an anomalously large coefficient of diffusion at these densities. The cause of the tail is probably to be found in a weak vortex pattern which a moving molecule apparently generates. If a molecule is moving along, say, the x -axis at a particular time then its very motion will tend to establish a pattern of motion in the neighbouring molecules which resembles a vortex ring with cylindrical symmetry about the x -axis. The motion of the molecules in this ring gives an impetus to the first molecule along the x -axis, thus tending to prolong its motion in that direction.²³ Such long tails in the c.f., and the complicated molecular motions which give rise to them, are clearly going to make it difficult to develop a statistical theory of transport for fluids of densities between those of the dense liquid and the dilute gas. That is, no early truncation of the memory function expansion is likely to do justice to the complexity of the motions.

The measurement of correlation functions for a real liquid is more difficult than their computer simulation. In Section 3 we saw that their spectra can be obtained from scattering experiments but these rarely cover a sufficiently complete range of k or ω for their successful Fourier inversion. If we want to study the one-molecule correlation functions then we must use incoherent neutron scattering, and so are restricted to substances containing atoms at least one of whose isotopes has a large incoherent cross-section. The best is the proton, with an incoherent cross-section of 79.7 barn and a coherent of 1.8 barn, and after that the best is apparently sodium for which both areas are 1.7 barn. For argon (incoherent 0.4 barn and coherent 0.5 barn) Dasannacharya and Rao²⁴ have obtained $G_s(\mathbf{r}, t)$ at 85 K, but only with an accuracy of ca. 15%. From this result we could go to the diffusion coefficient by calculating $\langle r^2 \rangle$ from equation (21), and then obtaining D from the limiting slope of Figure 4, or we can use the fact that if G_s at time t has a Gaussian shape (as they aver) then its width $w(t)$ is related to the velocity c.f. by^{5,13,25}

$$w(t) = \frac{2}{3} \int_0^t \langle \mathbf{v}(0) \cdot \mathbf{v}(t') \rangle (t - t') dt' \quad (22)$$

For liquid sodium the results are more extensive although, judging by the agreement between different workers,^{8,13} not necessarily more accurate. Figure 5 shows a spectrum of the velocity c.f., which resembles that for a liquid of Lennard-Jones molecules (Figure 2) more closely than either resemble the Lorentzian form predicted by a simple Langevin equation. The coefficient of diffusion calculated from the intercept of the spectrum at zero frequency is ca. $2.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, which is in only rough agreement with the experimental value²⁶ of $4.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

²³ B. J. Alder and T. E. Wainright, *Phys. Rev.*, 1970, **A1**, 18; T. E. Wainright, B. J. Alder, and D. M. Gass, *Phys. Rev.*, 1971, **A4**, 233; R. Zwanzig, in 'Statistical Mechanics - New Concepts, New Problems, New Applications', ed. S. A. Rice, K. F. Freed, and J. C. Light, University of Chicago Press, Chicago, 1972, p. 241; Papers by B. J. Alder and J. M. Deutch, and the discussion on them, in 'Transport Phenomena - 1973', ed. J. Kestin, American Institute of Physics, 1973.

²⁴ B. A. Dasannacharya and K. R. Rao, *Phys. Rev.*, 1965, **137**, A417.

²⁵ B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, 1970, **17**, 63; B. J. Berne, in 'Physical Chemistry, an Advanced Treatise', ed. D. Henderson, Academic Press, New York, 1971, Vol. 8B; B. J. Berne and D. Forster, *Ann. Rev. Phys. Chem.*, 1971, **22**, 563; R. T. Bailey, in 'Molecular Spectroscopy', ed. R. F. Barrow, D. A. Long, and D. J. Millen, (Specialist Periodical Reports). The Chemical Society, London, 1974, Vol. 2, p. 173.

²⁶ P. A. Egelstaff, 'Introduction to the Liquid State', Academic Press, London, 1967, p. 4.

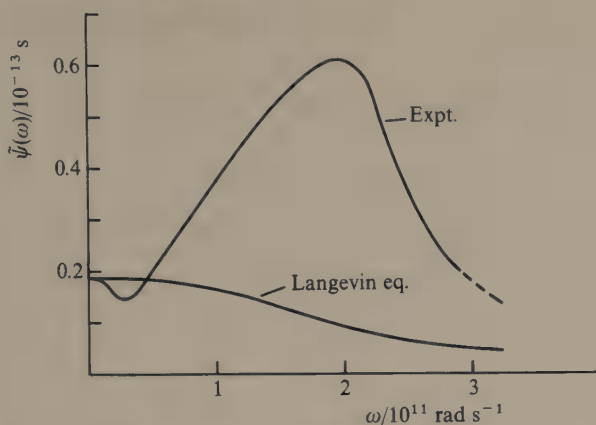


Figure 5 The experimental Fourier transform of the velocity c.f. for liquid sodium⁸ compared with the form of this function predicted by Langevin's equation

5 Absorption in Molecular Liquids

In this Section and the next two we describe how we can study the rotary motion of molecules by means of the bandshapes of their spectra, which are linked to orientational auto-correlation functions. Let \mathbf{u} be a unit vector along a convenient axis of the molecule (usually along the permanent dipole moment, if any), and \mathbf{J} the angular velocity vector, which is perpendicular to \mathbf{u} in a diatomic molecule. We shall use the following correlation functions; the first in this section, the second in Section 6 and the third in Section 7.

$$^{(\text{IR})} \psi(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$$

$$^{(\text{R})} \psi(t) = \frac{1}{2} \langle 3[\mathbf{u}(0) \cdot \mathbf{u}(t)]^2 - 1 \rangle \quad (23)$$

$$^{(\text{J})} \psi(t) = \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle / \langle \mathbf{J}^2(0) \rangle$$

Here (IR) stands for infra-red, and (R) for Rayleigh rather than Raman since we shall be considering scattered light that is symmetrically disposed about the exciting line and not about a line displaced from it.

The Fourier transform of $^{(\text{IR})} \psi(t)$ is related to the dielectric absorption^{27,28} that arises from the attempt of dipolar molecules to respond to a small perturbing electric field, which may oscillate over a wide range of frequencies. Energy is absorbed because they cannot follow the applied field \mathbf{F} instantaneously. More than fifty years ago Debye discussed this phenomenon in terms of a rotational Langevin equation, in which the torque on a dipole $\boldsymbol{\mu}$ at an angle θ to the field \mathbf{F} is opposed by a frequency-independent microscopic coefficient of friction ζ which arises from the force-fields of neighbouring molecules.

$$\boldsymbol{\mu} \times \mathbf{F} = -\zeta \dot{\boldsymbol{\theta}} \quad (24)$$

²⁷ N. E. Hill, A. G. Price, W. E. Vaughan, and M. Davies, 'Dielectric Properties and Molecular Behaviour', Van Nostrand Reinhold, London, 1969.

²⁸ S. Kielich, in 'Dielectric and Related Molecular Processes', ed. Mansel Davies, (Specialist Periodical Reports), The Chemical Society, London, 1973, Vol. 1, p. 192.

The Langevin equation per unit moment of inertia is then (cf. equation 8)

$$\ddot{\theta}(t) = -\zeta \dot{\theta}(t) + \Gamma(t) \quad (25)$$

where $\Gamma(t)$ is the random torque imposed on a molecule by the motion of its neighbours. If $\phi(t)$ is the angle between $\mathbf{u}(0)$ and $\mathbf{u}(t)$ then^{25,29}

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \langle \cos \phi(t) \rangle \quad (26)$$

These equations describe adequately the rotational dynamics, and so the absorption, up to field frequencies of ca. 10^{12} Hz. As we move into the far-i.r. region³⁰ of 10^{13} Hz (i.e., for molecular motion at times of 10^{-13} s) then the same limitations apply to these equations as applied before to the translational Langevin equation. An obvious weakness appears if the absorption is expressed in terms of $\alpha(\omega)$, the absorption coefficient per unit path length. Integration²⁹ of equation (25) gives an absorption coefficient $\alpha(\omega)$ proportional to $\omega^2(1 + \omega^2)^{-1}$, which means that at high frequencies $\alpha(\omega)$ has a plateau, and spectral transparency is not regained.

The trouble lies, as before, in the neglect of molecular inertia, and so the assumption that the random torque $\Gamma(t)$ has an infinitely small correlation time. Only then is ζ independent of time. Equation (25) is the truncation of the rotational equivalent of Mori's continued fraction⁶ (Section 2) so that the memory function is a peak at $t=0$;

$$^{(\text{IR})}M(t) = D\delta(t) \quad (27)$$

where D is a rotational diffusion coefficient equal to $kT\zeta/I$. If $\Gamma(t)$ is to be non-Gaussian,²⁵ and if ζ is to be a function of time, then we must generalize Langevin's equation, in the same way as we went from equation (8) to equation (12);

$$^{(\text{IR})}\dot{\psi}(t) = -\int_0^t ^{(\text{IR})}\psi(t-t') ^{(\text{IR})}M_0(t') dt' + \Gamma(t) \quad (28)$$

This equation has been used recently to describe the far-i.r. absorption of furan and chloroform.³¹ The memory function $^{(\text{IR})}M_0(t)$ which replaces the delta-function of the simple Langevin equation is the c.f. of the random torque

$$^{(\text{IR})}M_0(t) = \langle \Gamma(0) \cdot \Gamma(t) \rangle \quad (29)$$

Since $^{(\text{IR})}M_0(t)$ is itself a c.f. it has its own memory function $^{(\text{IR})}M_1(t)$ defined by the analogue of equation (13), and we can again extend the series indefinitely. Mori's continued fraction for the Laplace transform starts

$$^{(\text{IR})}\tilde{\psi}(p) = \frac{^{(\text{IR})}\tilde{\psi}(0)}{p + ^{(\text{IR})}\tilde{M}_0(p)} = \frac{^{(\text{IR})}\tilde{\psi}(0)}{p + ^{(\text{IR})}\tilde{M}_0(0)/(p + ^{(\text{IR})}\tilde{M}_1(p))} = \text{etc.} \quad (30)$$

Table 1 summarizes how this series can be used as a framework into which to fit some of the widely used models for molecular rotation. The rotational, like the transla-

²⁹ G. Wyllie, in ref. 28, p. 21; G. Williams, *Chem. Rev.*, 1972, **72**, 55.

³⁰ C. Brot, in 'Dielectric and Related Molecular Processes', ed. Mansel Davies, (Specialist Periodical Reports), The Chemical Society, London, 1975, Vol. 2, p. 1.

³¹ B. Quentrec and P. Bezot, *Mol. Phys.*, 1974, **27**, 879.

tional velocity c.f., is necessarily an even function of time,³² and has a Taylor expansion

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = 1 - \frac{t^2}{2!} \langle \dot{\mathbf{u}}^2(0) \rangle + \frac{t^4}{4!} \langle \ddot{\mathbf{u}}^2(0) \rangle - \dots \quad (31)$$

The mean angular velocity $\langle \dot{\mathbf{u}}^2(0) \rangle$ of a linear molecule is $2kT/I$. The mean square acceleration $\langle \ddot{\mathbf{u}}^2(0) \rangle$ comprises two terms; a radial or centripetal acceleration due to the fact that the vector \mathbf{u} is of fixed length, and a tangential acceleration. The first is independent of the molecular interactions and is $8(kT/I)^2$, and the second is $\langle \mathcal{O}^2(V) \rangle / I$ where $\mathcal{O}(V)$ is the torque that the environment exerts on the molecule *via* the intermolecular potential V . The substitution of these expressions into equation (31) gives the equation of motion of an ensemble of interacting molecules. The equation shows the value of the c.f. representation in isolating the short-time behaviour from that at long times. The former can be followed analytically but the latter can be obtained only by invoking statistical arguments which usually lead to an exponential tail in the c.f.

Gordon³² and others²⁵ have calculated the first few terms of the expansions of $^{(IR)}\psi(t)$, $^{(R)}\psi(t)$, and $^{(I)}\psi(t)$; each contains the torque, a functional of the intermolecular potential V , $\langle \mathcal{O}(V) \rangle$, or its time derivative. The true c.f. is even in time and Table 1 shows the degree to which particular models satisfy this condition. Gordon's M and J diffusion models are zeroth-order truncations of Mori's series and so have a term in t^3 , and all higher odd terms. In these models the torque is not defined at the moment of impact (*i.e.*, it becomes instantaneously infinite) and so although transparency is regained in the far-i.r. (as ω^{-2}), it is regained more slowly than is found experimentally³³ for many dipolar liquids, and for those solid phases in which translational freedom is lost but rotational is retained. More recently^{31,35} the truncation at $M_1(t)$ shown in the last section of Table 1 has been used to ensure evenness to t^4 . The torque $\langle \mathcal{O}(V) \rangle$ is now well-defined at all times although its derivative $\langle \dot{\mathcal{O}}(V) \rangle$, which is part of the term in t^6 , is not. This is because the truncation at $M_1(t)$ implies that the angular acceleration is randomized in direction at each impact, so that its derivative has an infinite singularity. The absorption spectrum $\alpha(\omega)$ is the Fourier transform of $^{(IR)}\psi(t)$ and behaves asymptotically as ω^{-4} at high frequency. It reduces³¹ to a Debye curve when $\omega^4 \ll \omega^2$, as is shown in Figure 6 where it is compared with experimental results³³ for liquids and rotationally-free solids. Further comparisons with experiment can be found in the papers of Quentrec and Bezot³¹ and Evans and Evans.³⁵

It is remarkable that, although the agreement of $\alpha(\omega)$ with the experimental results is good over several decades of frequency, the overall memory function, $^{(IR)}M(t)$, is even only to t^2 . This function is another equilibrium property and so should be even in time. One possible remedy would be to truncate Mori's series at

³² R. G. Gordon, *J. Chem. Phys.*, 1966, **44**, 1830; *Adv. Magn. Resonance*, 1968, **3**, 1; R. E. D. McClung, *J. Chem. Phys.*, 1972, **57**, 5478.

³³ I. W. Larkin, *J.C.S. Faraday Symposia*, 1972, **6**, 112; R. Haffmanns and I. W. Larkin, *J.C.S. Faraday II*, 1972, **68**, 1729; M. Evans, M. Davies, and I. W. Larkin, *ibid.*, 1973, **69**, 1011; I. W. Larkin, *ibid.*, 1973, **69**, 1278; I. W. Larkin and M. Evans, *ibid.*, 1974, **70**, 477; I. W. Larkin, *ibid.*, 1974, **70**, 1457; M. Evans, *ibid.*, 1975, **71**, 2051.

³⁴ F. Blot, C. Abbar, and E. Constant, *Mol. Phys.*, 1972, **24**, 241; F. Blot and E. Constant, *Chem. Phys. Letters*, 1973, **18**, 253; 1974, **29**, 618.

³⁵ G. J. Evans and M. Evans, *J.C.S. Faraday II*, 1976, **72**, in press.

Table 1 Some dynamical models in Mori's formalism

| Model and references | $(\text{IR}) M_n(t)$ | $(\text{IR}) M_n(p)$ | Description and comment | $(\text{IR}) \psi(t)$ |
|-------------------------------------|--|--|--|--|
| Debye 25, 27—30 | $(\text{IR}) M_0(t) = D \delta(t)$ | $(\text{IR}) M_0(p) = D$ | Molecular inertia neglected; infinitesimal angular displacement in infinitely short time. Used to describe dielectric absorption at low frequencies but leads to ■ 'Debye plateau' in the far-i.r. | $\exp(-t/\tau_M)$ where τ_M is the Debye relaxation time. Not ■ even function of t |
| Gordon M-diffusion 30, 32, 33 | $(\text{IR}) M_0(t) = (\text{IR}) M_0(0) e^{-\gamma_0 t}$ | $(\text{IR}) M_0(p) = \frac{(\text{IR}) M_0(0)}{p + \gamma_0}$ | Instantaneous elastic collisions perturb the rotation at random times. Angular velocity vector is randomized in direction; torque is infinite at impact. A slow return to transparency in the far-i.r. | This has a Taylor expansion $1 - at^2 + O(t^3)$ and so starts as an even function of t |
| Gordon J-diffusion 32, 34 | $(\text{IR}) M_0(t) = M_{FR}(t) e^{-\gamma_1 t }$ where $M_{FR}(t)$ is the memory function of ■ free rotator | | As for M-diffusion except that angular velocity is randomized in both direction and magnitude. An 'inertia-corrected' Debye model | A complicated function whose Taylor expansion has a term in t^3 |
| 25, 31, 35 | $(\text{IR}) M_1(t) = (\text{IR}) M_1(0) e^{-\gamma_1 t}$ | | Torque is always finite. Describes both low-frequency and far-i.r. absorption more satisfactorily than previous models. The past history of molecular movements and interactions influences future behaviour, i.e. a non-Markovian model | Taylor expansion is even to t^4 but contains a term in t^5 . Exponential at long times, oscillatory at short — a reflection of molecular libration, and the origin of the far-i.r. Poley absorption |

higher and higher order, but this introduces an inacceptably large number of averages $^{(IR)}M_2(0), \dots, ^{(IR)}M_n(0)$, which cannot be obtained analytically and which would therefore remain as phenomenological coefficients. A limitation of Mori's approach is that it does not give a natural picture of the long-time or hydrodynamic tail of the c.f. of angular velocity $^{(J)}\psi(t)$, as emphasized in many papers at a conference in Paris.³⁶ The long-time behaviour of $^{(J)}\psi(t)$ appears to go as $t^{-\frac{3}{2}}$, as for the translational case discussed in Section 4. Such a limit is expected also for $^{(IR)}\psi(t)$, at least for spherical tops, but this tail would distort the spectrum only on the low-frequency side of the Debye absorption.

It is natural to expect i.r. absorption associated with the rotation of a dipolar molecule in a liquid, but not so obvious that non-dipolar molecules also absorb in the far-i.r. and high microwave region.³⁷ This arises from the small, temporary, dipole induced in a normally non-polar molecule by the fluctuating fields of moving neighbours. The reciprocal of the half-width of the absorption band is of the order of the lifetime of the induced dipole, which is generally *ca.* 0.2×10^{-12} s. The associated c.f. is one of orientation coupled with interaction, and it falls to zero much more rapidly than its purely orientational dipolar counterpart $^{(IR)}\psi(t)$.

Mori's approximation injects a unity into the description of both permanent and induced dipolar absorption, as can be seen by the ease with which the truncation at M_1 , which was successful in reproducing the permanent dipole absorption (Figure 6), also reproduces the induced dipole absorption in a range of liquids from nitrogen to benzene (Figures 7 and 8). For these liquids both $M_0(0)$ and $M_1(0)$ are multi-molecular in origin since an isolated molecule would not absorb. Both averages are related to $\langle \mathcal{O}^2(V) \rangle$, although not in a simple way, and so can be used as rough probes for the change with pressure and temperature of the mean-square torque.³⁸

6 Depolarized Rayleigh Scattering—a Study of $^{(R)}\psi(t)$

We saw in Section 3 that light scattered from a monatomic liquid had two components, a Rayleigh line of the same frequency as the incoming light, and, surrounding it on either side, a pair of Brillouin lines shifted by an amount proportional to the speed of sound in the liquid. In a molecular liquid there is usually also a weak, very broad depolarized band, centred on the incident frequency which leads to the so-called Rayleigh wings. It is now generally agreed that this band arises from the re-orientation of single molecules, an interpretation which differs from that of collective (shear-wave) modes which prevailed³⁹ before the c.f. formalism was introduced about ten years ago. However, both mechanisms may be involved in the long-time tails on the c.f. $^{(R)}\psi(t)$ which molecular dynamic studies have shown to be present. As with the corresponding tails in the translational velocity c.f. (Section 4), these probably arise from a coupling of the motion, in this case orientational, of a single molecule with the hydrodynamic transverse velocity gradients.⁴⁰

³⁶ 'Molecular Motions in Liquids', ed. J. Lascombe, Reidel, Dordrecht, 1974.

³⁷ M. Davies, *Ann. Reports*, 1970, **67**, 65; M. Davies, G. W. F. Pardoe, J. Chamberlain, and H. A. Gebbie, *Trans. Faraday Soc.*, 1970, **66**, 273; G. W. F. Pardoe, *ibid.*, p. 2699; G. J. Davies, J. Chamberlain, and M. Davies, *J.C.S. Faraday II*, 1973, **69**, 1223; G. J. Davies and J. Chamberlain, *ibid.*, 1973, **69**, 1739; G. J. Davies and M. Evans, *ibid.*, 1975, **71**, 1275.

³⁸ G. J. Davies and M. Evans, *J.C.S. Faraday II*, 1976, **72**, in press.

³⁹ I. L. Fabelinskii, 'Molecular Scattering of Light', Plenum Press, New York, 1968.

⁴⁰ J.-L. Greffe, J. Goulon, J. Brondeau, and J.-L. Rivail, in ref. 36, p. 151.

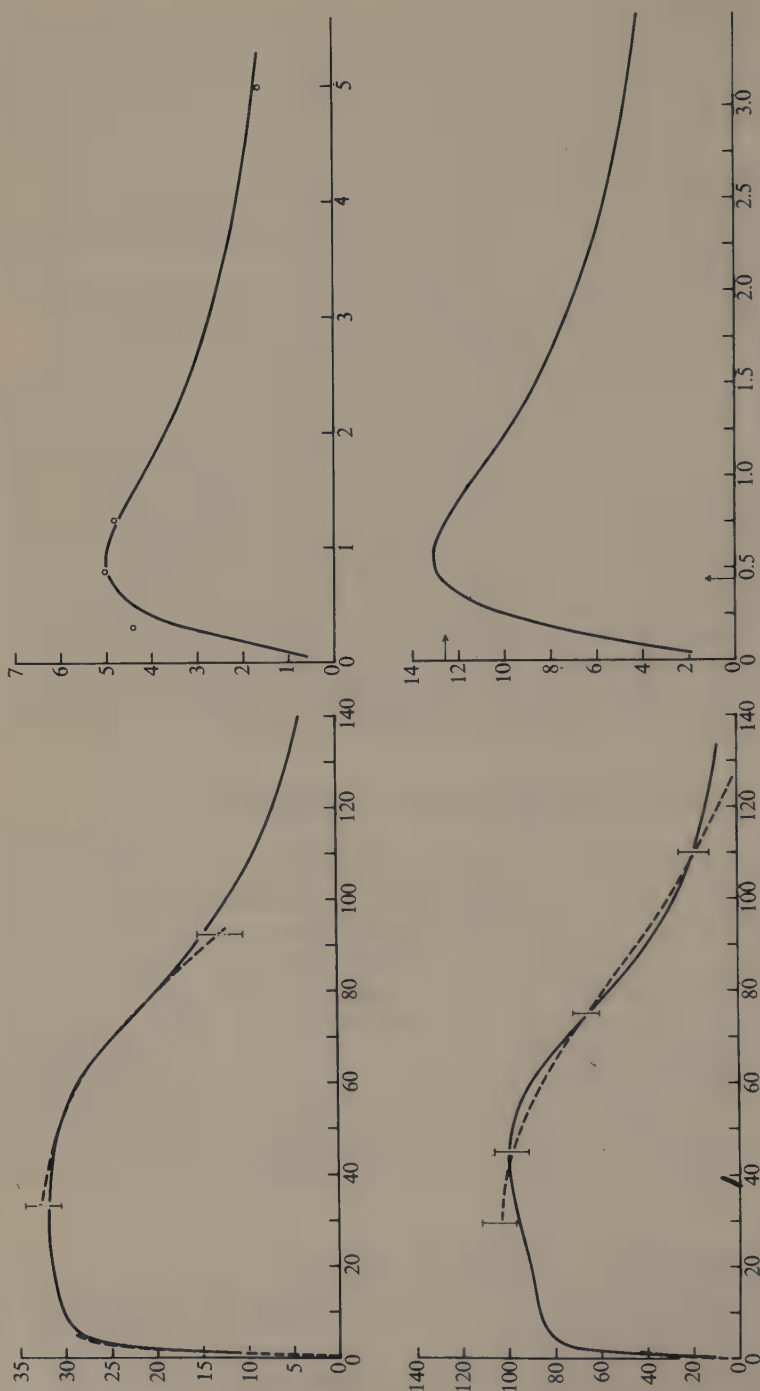


Figure 6 The absorption (top left) and dielectric loss (top right) of *t*-butyl chloride in the rotator solid phase at 238 K. The abscissae are wavenumbers (cm^{-1}) and the ordinates are α in nepers cm^{-1} and ϵ'' . The dashed lines are the experimental absorption³³ and the points the experimental measurements of dielectric loss in the microwave region.³³ The full lines are calculated from the truncation in the last line of Table 1. The lower figures are similar results for the absorption and loss in liquid $\text{Me}_2\text{CCINO}_2$ at 296 K. The arrows in the lower right-hand figure mark the position and intensity of the peak in the dielectric loss

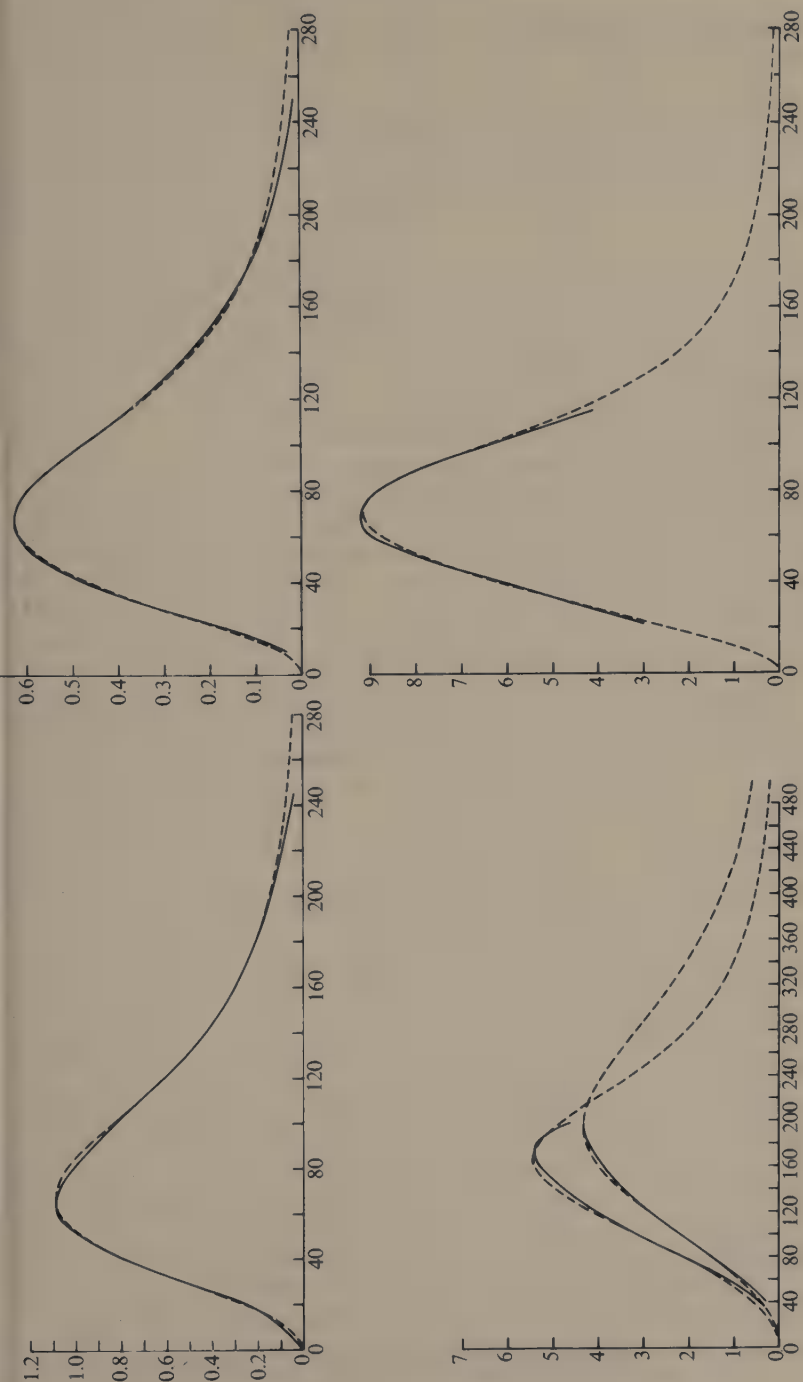


Figure 7 The absorption α in neper cm^{-1} for non-dipolar substances as a function of wavenumber in cm^{-1} . Liquid N_2 at 76.4 K (top left), liquid CO_2 at 273 K (top right), liquid CH_4 at 98 K (bottom left, the broader band), solid CH_4 at 77 K (bottom left, the narrower band), and liquid $(\text{CN})_2$ at 301 K (bottom right). The experimental results are shown by the full curves and the theoretical calculations, from the truncation in the last line of Table 1, by the dashed curves.

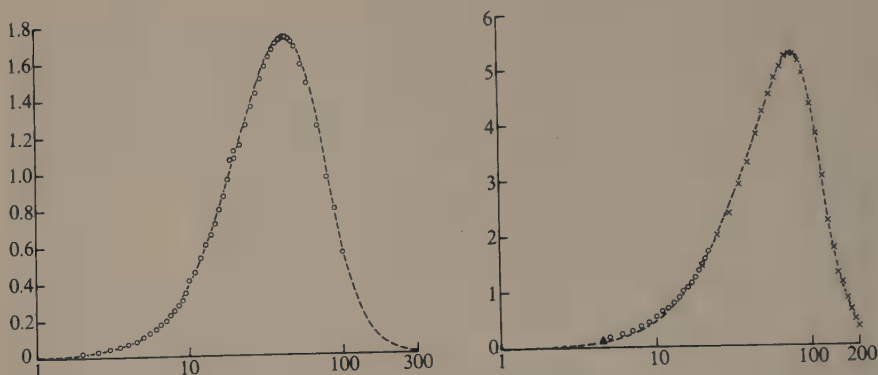


Figure 2 The absorptions³⁸ α in neper cm^{-1} as a function of wavenumber in cm^{-1} for the non-dipolar liquids CCl_4 (left) and C_6H_6 (right)

If the incoming light is travelling in the x -direction, if it is polarized in the z -direction (vertically), and is observed in the y -direction, polarized in the x -direction (horizontally) then the scattered spectrum is $I_{\text{VH}}(\omega)$, and it arises from a dipole induced in the x -direction by a field along the z -direction. Such a dipole is proportional to the xz -element of the electric polarizability of the scattering volume. For a system with isotropically polarizable molecules (e.g. CCl_4), this element is zero. Gordon³² showed in 1966 that this depolarized component is the Fourier transform of the average motion of the polarizability tensor and so, for self-correlation in a linear or symmetric top molecule, of the c.f. $^{(\text{R})}\psi(t)$. The depolarized light scattered from liquids with anisotropic polarizability arises from local fluctuations of the orientation from the random isotropic average. If it is assumed that the movement of neighbouring molecules is uncorrelated then the scattered intensity at frequency ω from the exciting line is

$$I_{\text{VH}}(\omega) \propto (\alpha_{\parallel} - \alpha_{\perp})^2 \int_{-\infty}^{\infty} {}^{(\text{R})}\psi(t) e^{-i\omega t} dt \quad (32)$$

This expression is similar to the quantal equation³² for the rotational absorption in the microwave and far-i.r. bands;

$$A(\omega) \propto \frac{\alpha(\omega)}{\omega[1 - \exp(-\hbar\omega/kT)]} \propto \mu^2 \int_{-\infty}^{\infty} {}^{(\text{IR})}\psi(t) e^{-i\omega t} dt \quad (33)$$

$I_{\text{VH}}(\omega)$ and $A(\omega)$ have quantitatively the same features. The low-frequency Lorentzian⁴¹ of the scattered light corresponds to the low-frequency Debye relaxation in dipolar absorption. This Lorentzian is imposed on a broader background which extends to ca. 100–150 cm^{-1} corresponding to the far-i.r. Poley absorption.^{27,30} Beyond this the intensity falls exponentially with frequency.

The Lorentzian behaviour at low frequencies implies that the long-time behaviour of both $^{(\text{IR})}\psi(t)$ and $^{(\text{R})}\psi(t)$ is exponential with relaxation times of τ_{M} and τ_{R} respectively, the reciprocals of the half-widths of the Lorentzians. Details of the

⁴¹ D. A. Pinnow, S. J. Candau, and T. A. Litovitz, *J. Chem. Phys.*, 1968, **39**, 347; H. Dardy, V. Volterra, and T. A. Litovitz, *J.C.S. Faraday Symposia*, 1972, **6**, 71; *J. Chem. Phys.*, 1973, **59**, 4491.

molecular motion are reflected in the deviations from the exponentials at short times, and give rise to an added background or shoulder in the scattered light, and to the Poley absorption in the i.r.

A simple comparison of τ_M with τ_R tells us something of the mechanism of re-orientation; for example whether it is by large rotational jumps or not.⁴² Thus if motion about an axis can be described by a model of rotational diffusion with individual time steps of a short time τ , then Hubbard's equation⁴³ links τ , τ_M , and τ_R

$$\tau = I/6kT\tau_R = I/2kT\tau_M \quad (34)$$

If the Rayleigh scattering is observed as a function of temperature⁴¹ then, in principle, the different contributions to the scattering can be assigned different energies of activation which can be compared with those obtained from viscosity and dielectric measurements. For the substituted benzenes⁴¹ good agreement with experiment can be obtained by attributing the spectrum of linearly anisotropic molecules to a single mechanism of re-orientation. However, the far wing of the Rayleigh scattering contains also information about intermolecular properties since a weak exponential scattering is observed here even with molecules with scalar polarizabilities⁴⁴ such as CCl_4 . Bucaro and Litovitz⁴⁵ used a simple binary-collision approach to model this scattering for spherically polarizable molecules. However, the spectra of anisotropic liquids show the same quasi-exponential tail and also a shoulder around $50\text{--}90\text{ cm}^{-1}$ which cannot be accounted for by this simple, distortional, binary mechanism.

After subtracting the collision-induced component of $^{(R)}\psi(t)$, Dardy *et al.*⁴¹ found that a molecule such as benzene behaves much as a free-rotator at short times. There is an average rotation of *ca.* 15° between collisions. The long-time behaviour of $^{(R)}\psi(t)$ is found to be exponential, reflecting the ultimate diffusional behaviour. It can be shown^{30,46} that the short-time behaviour of a c.f. is revealed in greater detail by an analysis of its second derivative; for example, $^{(R)}\ddot{\psi}(t)$ is related to the correlation of angular momenta and angular orientation. This c.f. shows^{42,46} that there is not a complete loss of memory during collisions in molecules like benzene and so the simple diffusion model which lies behind the Hubbard equation is inadequate.

The Rayleigh scattering has been observed also as a function of pressure⁴⁷ and from these measurements the change with density of $^{(R)}\psi(t)$ and $^{(R)}\ddot{\psi}(t)$ can be obtained. The mechanism of re-orientation appears to involve rotation which is randomly affected by collisions but it is a process which is not described accurately by the *J*-diffusion model. The c.f. $^{(R)}\ddot{\psi}(t)$ has a negative region and oscillates [as is well documented^{33,37} for $^{(IR)}\ddot{\psi}(t)$], thus showing that there is not a complete randomization of the angular velocity at each collision. There is also evidence that memory of

⁴² F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, 1972, **56**, 413.

⁴³ P. S. Hubbard, *Phys. Rev.*, 1963, **131**, 1155.

⁴⁴ J. P. McTague and G. Birnbaum, *Phys. Rev. Letters*, 1968, **21**, 661; W. S. Gornall, H. E. Howard-Lock, and S. P. Stoicheff, *Phys. Rev.*, 1970, **A1**, 1288.

⁴⁵ J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.*, 1971, **55**, 3846.

⁴⁶ T. Keyes and D. Kivelson, *J. Chem. Phys.*, 1972, **56**, 1057; *ibid.*, 1972, **57**, 4599; A. G. St. Pierre and W. A. Steele, *J. Chem. Phys.*, 1975, **62**, 2286.

⁴⁷ J. F. Dill, T. A. Litovitz, and J. A. Bucaro, *J. Chem. Phys.*, 1975, **62**, 3839; P. van Konynenburg and W. A. Steele, *ibid.*, p. 2301; M. Perrot, J. Devaure, and J. Lascombe, *Mol. Phys.*, 1975, **30**, 97.

one impact is carried through to the next, and beyond. The oscillations in $^{(R)}\ddot{\psi}(t)$ are most pronounced in strongly anisotropic molecules such as benzene, and suggest that such strong anisotropic forces lead towards molecular libration.³³ This mechanical anisotropy is accentuated at high molecular densities. The J -diffusion model is qualitatively adequate only for the simplest molecules, such as N_2 and CO .

From the Mori series for depolarized Rayleigh scattering we see that the truncation

$$^{(R)}M_0(t) = D_R \delta(t) \quad (35)$$

is equivalent to the Debye model of dielectric absorption, and leads to the Lorentzian,

$$I_{VH}(\omega) \propto (\alpha_{\parallel} - \alpha_{\perp})^2 D_R (D_R + \omega^2)^{-1} \quad (36)$$

which is adequate only at long times. The shoulder^{42,47} found at higher frequencies in moderately and highly anisotropic liquids can neither be described by a Lorentzian nor fitted by the distortional mechanism of Bucaro and Litovitz.⁴⁵

The truncation

$$^{(R)}M_0(t) = ^{(R)}M_0(0) \exp(-\gamma_0 t) \quad (37)$$

yields, on Fourier transformation of the corresponding $^{(R)}\psi(t)$, the scattering function of the M -diffusion model, which is proportional to ω^{-4} at high frequencies and reduces to a Lorentzian when $\omega^4 \ll \omega^2$. The equilibrium average $^{(R)}M_0(0)$ is still, for this model, a property of a single molecule (no torque involved); for a linear molecule it is $3kT/I$.

The limitations of the M - and J -diffusion models in their treatment of torque (Section 5), and the false assumption of complete randomization of angular velocity at each collision have been revealed by the measurements at high pressure. Thus the J -diffusion model is adequate for the Rayleigh scattering in liquid CO_2 up to 100 bar, but fails at higher pressures when the index n of the frequency dependence (ω^{-n}) changes to higher n at intermediate and high frequencies. This sharper asymptotic fall-off with ω suggests that the truncation

$$^{(R)}M_1(t) = ^{(R)}M_1(0) \exp(-\gamma_1 t) \quad (38)$$

might lead to a suitable function for $I_{VH}(\omega)$. A finite torque is now implied in $^{(R)}M_1(0)$; for a linear molecule

$$^{(R)}M_1(0) = \frac{\langle \mathcal{O}^2(V) \rangle}{24kTI} - \frac{5}{3} \left(\frac{kT}{I} \right) \quad (39)$$

The function $I_{VH}(\omega)$ is again Lorentzian at low frequencies but now has a peak²⁵ around 50 cm^{-1} , near the shoulder found by Dardy *et al.*⁴¹ in anisotropic liquids.

The complete spectrum of depolarized scattered light can be written as the sum of three terms;

$$I(\omega) = I_{VH}(\omega) + I_{COL}(\omega) + I_{VH-COL}(\omega) \quad (40)$$

where $I_{COL}(\omega)$ is the collisional part of the intensity observable in molecules with isotropic polarizability such as CCl_4 . The theoretical expressions from which the sign and magnitude of the cross-term can be calculated are only crude, but its neglect⁴²

does not seem to affect the consistency of the subsequent analysis of the results. In anisotropic molecules $I_{\text{VH}}(\omega)$ accounts for almost all the intensity and $I_{\text{COL}}(\omega)$ is restricted to the wings. Bucaro and Litovitz⁴⁵ predict

$$I_{\text{COL}}(\omega) \propto \omega^{12/7} \exp(-\omega/\omega_0) \quad (\omega > \omega_0) \quad (41)$$

where ω_0 is calculated from a chosen intermolecular potential, usually of the Lennard-Jones form. $I_{\text{COL}}(\omega)$ is a Lorentzian if $\omega < \omega_0$. The equivalent expression in the far-i.r.⁴¹ is

$$\alpha_{\text{COL}}(\omega) \propto \omega^{26/7} \exp(-\omega/\omega_0) \quad (\omega > \omega_0) \quad (42)$$

but this fits the results much less satisfactorily⁴⁸ than the anisotropic term shown in Figures 7 and 8.

Bucaro and Litovitz⁴⁹ emphasize the similarity between $I_{\text{COL}}(\omega)$ and the population-corrected dielectric loss factor in non-polar liquids, viz.

$$\epsilon''(\omega) \left[1 - \exp\left(\frac{\hbar\omega}{kT}\right) \right]^{-1}$$

They have shown that both are fairly well described by semi-empirical equations such as (41) and (42). Both have separate high- and low-frequency portions, whereas the generalized Langevin theory of Kubo, Mori, and others stresses that these peaks in the i.r. (or shoulders in the Rayleigh spectrum) are to be treated as part of the lower frequency orientational processes – a unifying formalism for both dipolar (anisotropic) and non-dipolar (isotropic) molecules. It would therefore seem to be fruitful to treat $I_{\text{COL}}(\omega)$ by invoking Mori's truncation at first-order, with both $^{(\text{R})}M_1(0)$ and $^{(\text{R})}M_0(0)$ as torque dependent parameters.

7 N.M.R. Spin-Rotation Relaxation—a Study of $^{(\text{J})}\psi(t)$

The relaxation of nuclear spins is determined by their coupling with the translational and rotational motions of the molecule. For a nucleus of spin $\frac{1}{2}$, the spin-rotation interaction of a linear molecule has a Hamiltonian of the form $-c\mathbf{I} \cdot \mathbf{J}$, where \mathbf{I} is the angular momentum of the nucleus, \mathbf{J} is that of the molecule, and c is the spin-rotation coupling constant.^{25,32} When this is the only part of the total energy which leads to relaxation of the spins then the spin-relaxation time T_1 is

$$\frac{1}{T_1} = \frac{c^2}{3\hbar^2} \int_{-\infty}^{\infty} \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle e^{-i\omega_0 t} dt \quad (42)$$

where $^{(\text{J})}\psi(t)$ is the third c.f. defined in equation (23), and ω_0 is the Larmor precession frequency. In a typical liquid ω_0^{-1} is of the order of 10^{-6} s, and this is so much longer than the time for the angular momentum c.f. to decay to zero (say, 10^{-11} s) that the exponential term in (42) can be put equal to unity.

For a linear molecule the expansion²⁵ of $^{(\text{J})}\psi(t)$ in powers of t^2 resembles those of the ratios $^{(\text{IR})}\ddot{\psi}(t)/^{(\text{IR})}\ddot{\psi}(0)$ and $^{(\text{R})}\ddot{\psi}(t)/^{(\text{R})}\ddot{\psi}(0)$. Gerschel, Darmon, and Brot⁵⁰ showed that the (IR) ratio oscillated at short times, and measurements of light scattering from

⁴⁸ M. Evans, *J.C.S. Faraday II*, 1975, **71**, 71.

⁴⁹ J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.*, 1971, **55**, 3585; T. A. Litovitz, in ref. 36, p. 613.

⁵⁰ A. Gerschel, I. Darmon, and C. Brot, *Mol. Phys.*, 1972, **23**, 317.

liquids at high pressures⁴⁷ have shown that the (R) ratio does also. There has been little if anything reported from n.m.r. studies of the full time dependence of $^{(J)}\psi(t)$, but Berne and Harp²⁵ have made computer calculations which show that it is negative for an interval of time if the pair potential is anisotropic. It remains positive and changes little over an interval of 10^{-12} s if the pair potential is of the Lennard-Jones form.

If there is no molecular interaction then $\langle \mathcal{O}^2(V) \rangle$ is zero, the c.f. $^{(J)}\psi(t)$ is unity, and its memory function $^{(J)}M(t)$ is zero. Hence $^{(J)}M(t)$ can be looked upon as a molecular memory of the interactions. In contrast, $^{(IR)}M(t)$ and $^{(R)}M(t)$ are non-zero decaying functions even in the absence of torque since there is always a distribution of frequencies of rotation. If $^{(J)}\psi(t)$ is, at any time, negative, then $^{(J)}M(t)$ must be non-zero; that is, a molecule retains some memory of its interactions. Berne and Harp²⁵ find that in simulated CO $^{(J)}M(t)$ goes almost to zero within 0.3×10^{-12} s, and that there is then a much slower decay, with a final positive tail. The time of 0.63×10^{-12} s is roughly that taken by a molecule to move from the centre of its 'cage' and meet one of its neighbours at the 'wall'.

An example of an n.m.r. study of spin-rotation relaxation is the work of Rigny and Virlet⁵¹ on the relaxation of the fluorine nuclei in UF_6 , WF_6 , and MoF_6 , all of which are liquid at temperatures little above room temperature. They are unusual in that, contrary to the behaviour of most liquids,⁵² the spin-rotation interaction is the dominant mechanism of relaxation even at temperatures well below the critical. The molecules retain their angular momentum for a long (correlation) time, but the rotation is not free since they can move only about 1 radian at 343 K before their angular momentum changes.

These conclusions are revealed by using the generalized Langevin equation which now takes the form

$$\dot{\mathbf{J}}(t) = - \int_0^t {}^{(J)}\mathbf{M}(t-t')\mathbf{J}(t') dt' + \boldsymbol{\Gamma}_J(t) \quad (43)$$

where $\boldsymbol{\Gamma}_J(t)$ is the random torque and \mathbf{M} the memory function. The associated spectrum is then

$$\begin{aligned} \frac{{}^{(J)}\tilde{\psi}(i\omega)}{\langle J^2(0) \rangle} &= \int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle e^{-i\omega_0 t} dt \\ &= {}^{(J)}\tilde{\psi}(0)[i\omega_0 + {}^{(J)}M(\omega_0)]^{-1} \end{aligned} \quad (44)$$

where ω_0 is the Larmor frequency of spin precession. This is again sufficiently small to be neglected so the exponential term is unity. That is, $\boldsymbol{\Gamma}_J(t)$ fluctuates so rapidly that its c.f., which is related to $^{(J)}M(\omega)$ by

$${}^{(J)}M(\omega) = \frac{1}{\langle J^2(0) \rangle} \int_0^\infty \langle \boldsymbol{\Gamma}_J(0) \cdot \boldsymbol{\Gamma}_J(t) \rangle e^{-i\omega t} dt \quad (45)$$

is a delta function. The simple Langevin equation is thus regained with $^{(J)}M$ independent of frequency. Therefore

$$\frac{1}{T_1} \propto \int_0^\infty {}^{(J)}\psi(t) dt \propto \frac{{}^{(J)}\tilde{\psi}(0)}{{}^{(J)}M} = {}^{(J)}\tilde{\psi}(0)\tau_J \quad (46)$$

⁵¹ P. Rigny and J. Virlet, *J. Chem. Phys.*, 1967, **47**, 4645.

⁵² J. G. Powles, in 'Molecular Relaxation Processes', ed. M. Davies, Academic Press, New York, 1966.

where τ_J is the angular momentum correlation time, inversely proportional to T_1 , the spin-rotation relaxation time. As the temperature is raised the torque fluctuates more rapidly, the 'friction' is reduced, and so T_1 decreases. It is found in practice that this decrease follows an Arrhenius law.²⁷

For spherical tops such as CH_4 , CF_4 , SF_6 , and the hexafluorides above, the contribution of spin-rotation interaction to the n.m.r. lineshape is comparable with, and greater than at high temperatures, that of spin-spin magnetic dipole interaction. The latter is the contribution to spin resonance relaxation from the interaction of a pair of identical nuclei in the same molecule of spin quantum s , and a separation defined by the vector \mathbf{r} and the scalar distance b . The spin-spin relaxation time is

$$[T_2(\omega)]_{ss}^{-1} \approx \frac{2\gamma^4 \hbar^2 s(s+1)}{b^6} \int_0^\infty \langle \mathbf{r} \rangle \psi(t) dt \quad (47)$$

where γ is the gyromagnetic ratio. This relaxation time provides therefore a method of measuring the area under the $\langle \mathbf{r} \rangle \psi(t)$ curve, which is a correlation time and is to be compared with a diffusion coefficient in the translational case, equation (6). It does not, however, tell us anything about $\langle \mathbf{r} \rangle \psi(t)$ itself as a function of time. Such n.m.r. results can be compared usefully³⁰ with those of dielectric measurements,^{27,28} particularly at temperatures near the triple point where rotational diffusion might be a useful concept. At the boiling point and at higher temperatures the mechanism of reorientation is generally interpreted with the help of the spin-rotation component of T_1 , thus taking advantage of the increased periods of rotation. The principal interest of such work is to study any anisotropy of motion; sometimes the rotation is almost free about one axis and diffusional about another perpendicular to it.⁵³

The integral of $\langle \mathbf{r} \rangle \psi(t)$ over all time defines a correlation time τ_R . In the limit of rotational diffusion this is related to τ_J by Hubbard's equation,⁴³

$$\tau_R \tau_J = I/6kT \quad (48)$$

and in the limit of a rarely perturbed free spherical-top rotation by

$$\tau_R = \tau_J/5 \quad (49)$$

For the intermediate region McClung³² has discussed the relation between τ_R and τ_J for spherical tops in terms of the M - and J -diffusion models. These approach the limits of equations (48) and (49) when τ_J is very small and very large. Sillescu has extended⁵⁴ the Debye model of Brownian motion and the random jump model²⁹ of rotation to take account of temporal fluctuations in their rates. Further developments in the use of n.m.r. in this field can be found in the comprehensive reports edited by Harris.⁵⁵

We conclude by applying the formulation in terms of memory functions to spin resonance relaxation. From the equipartition of kinetic energy over two degrees of

⁵³ D. K. Green and J. G. Powles, *Proc. Phys. Soc.*, 1965, **85**, 87; T. T. Bopp, *J. Chem. Phys.*, 1967, **47**, 3621; D. E. Woessner, B. S. Snowden, and E. T. Strom, *Mol. Phys.*, 1968, **14**, 265; J. Jones and T. M. Di Gennaro, *J. Chem. Phys.*, 1969, **50**, 2392; A. A. Marryot, T. C. Farrar, and M. S. Malmberg, *ibid.*, 1971, **54**, 64.

⁵⁴ H. Sillescu, *J. Chem. Phys.*, 1971, **54**, 2110.

⁵⁵ 'Nuclear Magnetic Resonance', ed. R. K. Harris, (Specialist Periodical Reports), The Chemical Society, London, 1971-1975, Vols. 1-4.

rotational freedom we have

$$kT = \langle J^2(0) \rangle / 2I \quad (50)$$

so that

$$\tau_J = \int_0^\infty {}^{(J)}\psi(t) dt \quad (51)$$

When ${}^{(J)}M$ and ${}^{(R)}M$ are both delta functions we have

$$\begin{aligned} {}^{(J)}\psi(t) &= e^{-t/\tau_J} \\ {}^{(R)}\psi(t) &= e^{-t/\tau_R} \end{aligned} \quad (52)$$

and τ_J and τ_R are linked by Hubbard's relation.

The mean field of force due to the neighbours tends to hold a given molecule in a fixed orientation for a variable time while superimposed on this time-smoothed field is a rapid fluctuation due to the actual molecular motions. This is approximated in Brownian theory by a random torque of simple character superimposed on a steady orientating field. If the constraining field is strong the molecule moves as a damped gyrostatic pendulum. If the constant is highly anisotropic the motion about one axis may approach free rotation. If the molecule is a spherical top its components of rotation behave independently. All these different modes are not describable by a simple exponential c.f. and the introduction of memory functions will probably lead to more satisfactory descriptions. Thus

$${}^{(J)}M_0(t) = {}^{(J)}M_0(0) \exp(-t/\tau_J') \quad (53)$$

is likely to lead to a better account of the dependence of the correlation time τ_J on temperature. In the M -diffusion model the product $\tau_J\tau_R$ goes through a minimum, dependent on $\langle \mathcal{O}^2(V) \rangle$, which is more realistic than Hubbard's relation, equation (48). With the truncation

$${}^{(J)}M_1(t) = {}^{(J)}M_1(0) \exp(-t/\tau_J'') \quad (54)$$

we have that $(T_1^{-1})_{SR}$ depends both on $\langle \mathcal{O}^2(V) \rangle$ and its time-derivative, so that the product $\tau_J\tau_R$ might behave ever more realistically. These applications have, however, still to be explored.

3 Liquid Crystals

By T. E. FABER

Department of Physics, The Cavendish Laboratory, Cambridge CB5 0HE
and

G. R. LUCKHURST

Department of Chemistry, The University, Southampton SO9 5NH

1 Introduction

Liquid crystals are a state of matter existing between the crystal and the amorphous liquid phases. At the microscopic level the characteristic property of a liquid crystal is the existence of long-range orientational order, in contrast with the short-range order typical of liquids. This ordered phase may be obtained from certain solids by heating and also destroyed by further heating; such liquid crystals are known as thermotropic. However, various solids may also be made to yield an orientationally ordered phase by the addition of the appropriate solvent; the resultant phase is known as a lyotropic liquid crystal. Although these two classes of liquid crystals have certain features in common, we shall be concerned largely with thermotropic liquid crystals in this Report.

The behaviour of liquid crystals stems from molecular interactions, both with each other and with external fields; in this sense all of their properties are molecular. However, many of the bulk properties are adequately described by continuum mechanics, which does not need to refer to the existence of molecules. This Report is therefore divided, somewhat arbitrarily, into two parts; the second of these deals with continuum studies of liquid crystals while the first considers other aspects, which are loosely described as molecular. We shall not, therefore, describe their applications in electro-optic display devices or as solvents in spectroscopy; neither will we refer to the synthesis of new liquid crystals.

This is the first account of thermotropic liquid crystals to appear in *Annual Reports*, even though this fascinating state of matter was discovered over eighty years ago. Consequently, although much of the literature surveyed appeared in 1975, we shall also refer to earlier publications when this seems appropriate. A number of texts on liquid crystals are available; these include the pioneering account by Gray,¹ the masterly treatise on their continuum behaviour by de Gennes,² and the more recent volumes edited by Gray and Winsor.³ The liquid-crystal state seems to have come of age, for it now merits a series describing recent advances in both our

¹ G. W. Gray, 'Molecular Structure and the Properties of Liquid Crystals', Academic Press, New York, 1962.

² P. G. de Gennes, 'The Physics of Liquid Crystals', Oxford University Press, 1974.

³ 'Liquid Crystals and Plastic Crystals', Vols. 1 and 2, ed. G. W. Gray and P. A. Winsor, Ellis Horwood Ltd., Chichester, 1974.

understanding and application of liquid crystals.⁴ Two general reviews of thermotropic liquid crystals have appeared recently.^{5,6} In addition, the RCA Review contains a number of good, in-depth, accounts of many specialized areas of liquid crystals; these include the molecular field theories of nematic⁷ and smectic A phases,⁸ the hard-rod mesophase,⁹ the determination of order parameters,¹⁰ continuum theory,¹¹ and their optical properties.¹²

The number of papers concerned with liquid crystals continues to grow, and it would be impossible to review all of these in the space available. We have therefore selected those publications which we believe to be of particular importance as well as close to our own interests.

PART I: Molecular Behaviour

2 Orientational Order

A complete description of both the orientational and spatial order in a liquid crystal is provided by a hierarchy of distribution functions which give the probability of finding clusters of molecules with particular positions and orientations. The simplest of these is the singlet orientational distribution function, but even this has proved to be particularly elusive. The singlet distribution can be determined for a paramagnetic spin probe dissolved in a supercooled nematic mesophase¹³ but has not been obtained for a pure mesophase. The singlet distribution for uniaxial phases may be expanded in terms of spherical harmonics with expansion coefficients proportional to the orientational order parameters. For rigid, cylindrically symmetric molecules this expansion reduces to a sum of Legendre functions

$$p(\theta) = \sum_{L(\text{even})} \left(\frac{2L+1}{2} \right) \bar{P}_L P_L(\cos \theta), \quad (1)$$

where θ is the angle between the molecular symmetry axis and the director. The series is slowly convergent, and so many order parameters \bar{P}_L would be required to yield the true distribution. Unfortunately only the first parameter, \bar{P}_2 , may be determined with any certainty; in principle, the next order parameter \bar{P}_4 may be obtained from Raman light-scattering experiments, but as we shall see, there is some controversy as to the reliability of these values. In the following sections we shall discuss the determination and interpretation of the order parameters \bar{P}_2 and \bar{P}_4 for the various liquid-crystal phases.

Nematics. Rigid Rod-like Molecules. Provided we are prepared to assume that the molecules constituting liquid crystals are rigid and possess a three-fold or higher symmetry axis, then a wide variety of techniques is available to determine \bar{P}_2 . These include measurement of the partially averaged diamagnetic susceptibility

⁴ 'Advances in Liquid Crystals', Vol. 1, ed. G. H. Brown, Academic Press, New York, 1975.

⁵ M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.*, 1974, **46**, 4.

⁶ G. Durand and J. D. Litster, *Ann. Rev. Mater. Sci.*, 1973, **3**, 269.

⁷ P. J. Wojtowicz, *RCA Rev.*, 1974, **35**, 118.

⁸ P. J. Wojtowicz, *RCA Rev.*, 1974, **35**, 388.

⁹ P. Sheng, *RCA Rev.*, 1974, **35**, 132.

¹⁰ E. B. Priestley, *RCA Rev.*, 1974, **35**, 144.

¹¹ P. Sheng, *RCA Rev.*, 1974, **35**, 408.

¹² E. B. Priestley, *RCA Rev.*, 1974, **35**, 584.

¹³ P. Krebs and E. Sackmann, *Mol. Phys.*, 1972, **23**, 437.

tensor, dielectric tensor, and refractive index tensor;¹⁴ the order parameter then occurs in the relationship between these tensors and the appropriate molecular parameters. The form of this relationship is well defined for the diamagnetic susceptibility, although there are considerable difficulties with the refractive index because the magnitude of the internal electric field is still the subject of some debate. There are those who prefer the Vuks formulation,¹⁵ whereas others prefer the more acceptable Neugebauer prescription,¹⁶ although the justification for either approach seems to be largely empirical. Despite the potential uncertainty in the order parameter extracted from measurements of refractive index, there has been some effort to improve the accuracy with which the birefringence can be determined.^{16,17} A more reliable technique is provided by observation of the dipolar splitting in the ¹H n.m.r. spectrum, although, under low resolution, only one order parameter may be determined.¹⁸

The results provided by these various methods may differ in the fine detail, but all agree that at the nematic-isotropic transition \bar{P}_2 is ca. 0.4, and it increases to approximately 0.7 at 40 °C below the transition. The basic features of these results are adequately accounted for by the Maier-Saupe theory, and the deviations from this theory are explained by employing a more general anisotropic intermolecular potential.⁷ This success is surprising because, by analogy with normal liquids, strong repulsive forces might be expected to play a dominant role in determining the molecular organization, whereas the theory employs a relatively weak potential. The unimportance of the repulsive part of the anisotropic potential is further supported by approximate statistical mechanical theories, such as the Onsager approach,⁹ which show that although an order-disorder transition is predicted for hard particles, the order parameter \bar{P}_2 of 0.84 at the transition is much too large. Other approximations, based on lattice models, lead to similar discrepancies when compared to the behaviour of real nematics. Of course, this failure could always be ascribed to the approximations rather than to the inappropriateness of the repulsive potential. The need for approximations in statistical mechanical calculations of dense ensembles may often be removed by resorting to the powerful computer-simulation techniques. Thus Vieillard-Baron's Monte Carlo calculation for an ensemble of spherocylinders, with length to breadth ratio of 3, is particularly important.¹⁹ Temperature plays no role in determining the static properties of hard particles, and so the system is studied as a function of the density, which is defined as the number density multiplied by the molecular volume. No evidence was found for an order-disorder phase transition even at densities as high as 0.54, whereas the scaled particle theory predicts a transition for a density of 0.518.²⁰ The absence of a phase transition is particularly disappointing, especially for the proponents of the repulsive potential. However, it may be that the system has not come to equilibrium because the particles become locked in unrealistic configurations. It may therefore be significant that a preliminary molecular dynamics configuration for ellipsoids interacting with a continuous hard

¹⁴ Y. Poggi, J. Robert, and J. Borel, *Mol. Cryst. Liquid Cryst.*, 1975, **29**, 311.

¹⁵ R. Chang, *Mol. Cryst. Liquid Cryst.*, 1975, **30**, 155.

¹⁶ H. S. Subramanyam, C. S. Prabha, and D. Krishnamurti, *Mol. Cryst. Liquid Cryst.*, 1974, **28**, 201.

¹⁷ W. Kuczynski and B. Stryja, *Mol. Cryst. Liquid Cryst.*, 1975, **31**, 267.

¹⁸ E. Boilini and S. K. Ghosh, *J. Appl. Phys.*, 1975, **46**, 78.

¹⁹ J. Vieillard-Baron, *Mol. Phys.*, 1974, **28**, 809.

²⁰ M. A. Cotter and D. E. Martire, *J. Chem. Phys.*, 1970, **52**, 1909.

potential does yield an orientationally ordered phase.²¹ However, like the approximate theories, this calculation also gives an order parameter \bar{P}_2 which is unrealistically large.

The molecular field approximation is most reliable when applied to the long-range properties of a mesophase; as a consequence there is some interest in seeing if the Maier-Saupe-like theories are as successful in predicting \bar{P}_4 as in accounting for \bar{P}_2 . Since most anisotropic molecular properties transform under rotation as second rank spherical harmonics, the majority of experiments can only provide \bar{P}_2 . However, the intensity of light scattered in a Raman experiment is proportional to the mean-square polarizability, and so depends on the order parameter \bar{P}_4 as well as \bar{P}_2 . The theoretical relationship between the scattered intensity and \bar{P}_4 is quite straightforward,²² although considerable precautions must be taken in the spectral analysis, especially if the contribution of director fluctuations to the scattering is to be avoided. The technique has been applied to 4'-n-heptyl-4-cyanobiphenyl, using the cyano vibration, which is well removed from other molecular vibrations.²³ The parameter \bar{P}_4 is found to be lower than that predicted by either the Maier-Saupe theory or the Humphries-James-Luckhurst extension. The departure of \bar{P}_4 from the predicted values is still more marked for a mixture of 4-n-butyloxybenzylidene-4'-cyanoaniline and 4-methoxybenzylidene-4'-n-butyraniline, where negative values of \bar{P}_4 have been determined.²⁴ The failure of theory is still unexplained, but the discrepancy could stem from error in the experimental values of \bar{P}_4 . This view is supported by linewidth variations in the e.s.r. spectra of a spin probe dissolved in the nematic mesophase of Merck Phase IV²⁵ which give values of \bar{P}_4 in support of the Maier-Saupe theory. The order parameter \bar{P}_4 is available from such measurements because the linewidths depend on the mean-square value of the relevant magnetic tensors, which are also second rank.^{26,27} Clearly, further experimental investigations employing both techniques are required, preferably of the same system, before we can be certain of either the success or failure of the simplest molecular field theories.

Deviations from Cylindrical Symmetry. Of course, the molecules of most mesogens are neither cylindrically symmetric nor rigid, as is so often supposed. Since the molecules do not possess a three-fold or higher symmetry axis, the single order parameter \bar{P}_2 must be replaced with the Saupe ordering matrix, defined by:

$$S_{ab} = \overline{(3 \cos \theta_a \cos \theta_b - \delta_{ab})} / 2 \quad (2)$$

where θ_a is the angle between the molecular axis a and the director. There has been one attempt to determine S for a nematogen,²⁸ but this was not entirely satisfactory because it involved the combination of results from different experiments. The reason for this lack of detail is quite straightforward, for techniques (such as measurement of the partially averaged refractive index tensor) only provide a single

²¹ J. Kushick and B. J. Berne, *J. Chem. Phys.*, 1976, **64**, 1362.

²² E. B. Priestley and P. S. Pershan, *Mol. Cryst. Liquid Cryst.*, 1973, **23**, 369.

²³ J. P. Heger, *J. Phys. (Paris)*, 1975, **36**, L-209.

²⁴ S. Jen, N. A. Clark, P. S. Pershan, and E. B. Priestley, *Phys. Rev. Letters*, 1973, **31**, 1552.

²⁵ G. R. Luckhurst and R. Poupko, *Chem. Phys. Letters*, 1974, **29**, 191.

²⁶ G. R. Luckhurst, M. Setaka, and C. Zannoni, *Mol. Phys.*, 1974, **28**, 49.

²⁷ G. R. Luckhurst, R. Poupko, and C. Zannoni, *Mol. Phys.*, 1975, **30**, 499.

²⁸ R. Alben, J. R. McColl, and C. S. Shih, *Solid State Comm.*, 1972, **11**, 1081.

piece of independent information and so cannot be expected to yield the five independent elements of the ordering matrix. Thus most experiments can give some average of S or, if the appropriate molecular interaction is cylindrically symmetric, one of its components. The complete matrix can be measured by n.m.r. spectroscopy, and this is part of a standard procedure for determining the geometry of solutes dissolved in a liquid-crystal solvent.²⁹ The same approach cannot be readily applied to a pure mesophase because the large number of dipolar interactions make it virtually impossible to resolve the complex ^1H n.m.r. spectrum. One solution to this problem is to replace certain protons by deuterons. Then the proton spectrum may be readily resolved after decoupling any deuteron-proton interactions. A successful analysis of the spectrum would then yield several partially averaged dipolar interactions, from which S can be determined. Although the proton spectra of partially deuteriated mesogens have been reported, there was no attempt either to simplify the spectra or to obtain a quantitative analysis.³⁰ Alternatively, the ^2H n.m.r. spectrum may be recorded; this is usually dominated by pairs of quadrupole-split lines from each deuterium, with some secondary structure from dipolar splittings. This technique has been applied to perdeuterio-4,4'-dimethoxyazoxybenzene, and both the partially averaged quadrupole splittings and dipolar coupling between the *ortho*-deuterons were obtained.³¹ The analysis of these splittings provides useful geometrical information but cannot give the ordering matrix, because the coupling between nuclei in different rings was too small to be resolved. Consequently, only the local ordering matrix for each ring could be determined, and these are found to be essentially cylindrically symmetric about the *para* axis, presumably because of internal rotation about this axis.

Since the molecules constituting nematogens are biaxial, there is the possibility that the mesophase itself might also be biaxial. The factors influencing the transition from a uniaxial to a biaxial nematic phase have been studied in some detail, using a variety of theoretical approaches. However, such a transition has yet to be observed; nonetheless, it is important to see how the molecular biaxiality will influence the properties of the uniaxial mesophase. Straley³² has tackled this problem for an ensemble of hard rectangular particles, but, as we have seen, the use of a repulsive potential may well invalidate the quantitative aspects of his calculation. A comparable theory has been reported which employs a general expansion of the pair potential for molecules of arbitrary shape.³³ The number of parameters in the resultant pseudopotential is reduced by restricting the summation to second-rank interactions and further assuming that the remaining coefficients may be equated with those expected for dispersion forces. The pseudopotential, parametrized in this way, contains two arbitrary parameters; one of these is proportional to the nematic-isotropic transition temperature while the other is related to the deviation of S from cylindrical symmetry. By using the data available for the nematogen 4,4'-dimethoxyazoxybenzene it is possible to predict the temperature dependence of the major element of S , at constant volume, in excellent agreement with experiment.³³

²⁹ J. W. Emsley and J. C. Lindon, 'NMR Spectroscopy using Liquid Crystal Solvents', Pergamon Press, Oxford, 1975.

³⁰ J. J. Visintainer, E. Bock, R. Y. Dong, and E. Tomchuk, *Canad. J. Phys.*, 1975, **53**, 1483.

³¹ P. Diehl and A. S. Tracey, *Mol. Phys.*, 1975, **30**, 1917.

³² J. P. Straley, *Phys. Rev. (A)*, 1974, **10**, 1881.

³³ G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Segre, *Mol. Phys.*, 1975, **30**, 1345.

Departures from predictions of the Maier-Saupe theory appear to be attributable to deviations from molecular cylindrical symmetry, but more accurate measurements of the total ordering matrix are required before we can be certain of the success claimed for the theory.

Non-rigid Molecules. Although there is scant experimental support for deviations of S from cylindrical symmetry, there is ample evidence for the profound influence of molecular non-rigidity. For example, the flexible alkyl chains which form a vital part of many mesogens are known to be responsible for the alternation in the nematic-isotropic transition temperature along an homologous series.^{1,3} This odd-even effect can be reconciled with the Maier-Saupe theory because the molecular interaction parameter is expected to alternate when averaged over the various chain configurations. However, the theory cannot explain the observed alternation in the entropy of transition, which is predicted to be constant. Marčelja was the first to develop a quantitative theory of such effects by specifically including the influence of the chain configurations on the intermolecular potential.³⁴ He proposed a pseudopotential which contains terms similar in form to the Maier-Saupe potential:

$$U(\theta_i) = -\sum_j V_{ij} \bar{P}_2^{(j)} P_2(\cos \theta_i) \quad (3)$$

where θ_i is the angle between the director and the supposed symmetry axis of the i^{th} unit. The order parameter for the j^{th} unit is denoted by $\bar{P}_2^{(j)}$ and the coefficients V_{ij} are related to the strength of the interaction between various units; these are usually the rigid aromatic core and the flexible alkyl chains. Marčelja then includes another term in the total pseudopotential to represent the dependence of the internal energy on the chain configuration. The resulting single-particle pseudopotential is then employed to determine the various order parameters, from the usual consistency equations, as well as the Helmholtz free energy, to obtain the transition temperature. Since the orientation of a unit in the alkyl chain depends on that of the rigid core, the total number of distinct chain configurations is unmanageably large; this number is reduced by restricting the rigid core to either three or five configurations. Despite this drastic approximation, the calculated alternation in both the transition temperatures and entropy of transition is in agreement with experiment.

The complexity of Marčelja's calculations tends to obscure those factors which are basically responsible for the various odd-even effects that are observed for most homologous series. This has prompted Pink to simplify Marčelja's theory;³⁵ the philosophy of his simplification is to treat the interactions of the alkyl chains both with each other and with the rigid aromatic core as perturbations. This has the advantage that averages over the chain configurations may be evaluated for a single particle in the absence of the molecular field; some influence of the field is in fact retained because configurations outside a cylinder generated by rotating an all-*trans* configuration of the chain are ignored. Despite some of the questionable assumptions necessary for the simplified theory, its predictions are comparable to those of the Marčelja theory, and hence in reasonable accord with experiment.

The two theories also predict that the order parameter \bar{P}_2 for the rigid core, evaluated at the transition temperature, should exhibit an odd-even effect. N.m.r. spectroscopy provides virtually the only method for testing this prediction. For

³⁴ S. Marčelja, *J. Chem. Phys.*, 1974, **60**, 3599.

³⁵ D. A. Pink, *J. Chem. Phys.*, 1975, **63**, 2533.

example, if the ordering matrix for the rigid unit is cylindrically symmetric then \bar{P}_2 could be determined from the dipolar splitting between the *ortho*-protons.³ An alternative route has been proposed by Pines and Chang;³⁶ this involves measurement of the ^{13}C n.m.r. spectrum from which the dipolar interaction with protons has been removed by noise decoupling. The remaining spectrum is particularly simple because each nucleus in the carbon skeleton can only contribute one line, whose frequency is determined by the partially averaged chemical-shift tensor and hence by the ordering matrix. This technique has been applied to the homologous series of 4,4'-di-n-alkoxyazoxybenzenes; unfortunately, no attempt was made to see if \mathbf{S} for the rigid core was cylindrically symmetric, and so only the order parameter at the transition was obtained for this series.³⁷ The order parameter was found to exhibit an odd-even effect, as predicted, with the maximum value of 0.455 found for the ethoxy-derivative and the minimum value of 0.365 observed for propyloxy. These results reveal that the quantitative aspects of Marčelja's theory are not quite so satisfactory, since the predicted maximum and minimum values are 0.455 and 0.399.³⁴

The Marčelja theory, but not Pink's simplification, may also be used to calculate the order parameters of the methylene groups along an alkyl chain. As we might have anticipated, these order parameters may be determined from the ^2H n.m.r. spectrum of the mesogen with deuteriated chains.^{38,39} The spectrum is dominated by a series of doublets, each of which come from the methylene groups or the terminal methyl group. The unambiguous assignment of a splitting to a particular group is impossible in the absence of specifically deuteriated mesogens, but it seems reasonable to suppose that the order parameter decreases along the chain. The results shown in Figure 1 for 4-cyano-4'-n-pentylbiphenyl,³⁹ terephthalylidene-bis(4-n-butylaniline),³⁸ and 4-n-butyloxybenzylidene-4'-n-octylaniline³⁸ were obtained with this assumption. The behaviour of the chains in these compounds shows similar trends, and is in qualitative agreement with Marčelja's calculations for 4,4'-di-n-octyloxyazoxybenzene,³⁴ although values are not yet available for the compounds studied. An alternative technique is to attach a paramagnetic group, such as 2-N-oxy-3,3-dimethyloxazolidine, at specific positions along the chain and to determine the ordering matrix for this group from the partially averaged g and hyperfine tensors. This approach has been used with several 4,4'-dialkyloxyazobenzenes dissolved in the smectic B and C phases of 4,4'-di-n-octadecyloxyazoxybenzene;⁴⁰ the order parameter is found to decrease along the chain in the manner similar to that shown in Figure 1. However, the order parameters exhibit a more pronounced odd-even effect which may be attributed to the perturbing influence of the spin label on the configurations adopted by the chain.

The orientational order in a mesophase makes it possible to observe a n.m.r. dipolar echo following an in-phase pulse sequence.⁴¹ The echo amplitude exhibits a gaussian dependence on the time τ between 90° pulses:

$$E(\tau, 90^\circ) = E(0, 90^\circ) \exp \left\{ -\frac{1}{2} M_2 \tau^2 \right\} \quad (4)$$

³⁶ A. Pines and J. J. Chang, *Phys. Rev. (A)*, 1974, **10**, 946; B. Clin, *Compt. rend.*, 1975, **280**, C, 73.

³⁷ A. Pines, D. J. Ruben, and S. Allison, *Phys. Rev. Letters*, 1974, **33**, 1002.

³⁸ B. Deloche, J. Charvolin, L. Liebert, and L. Strzelecki, *J. Phys. (Paris)*, 1975, **36**, Cl-21.

³⁹ J. W. Emsley, J. C. Lindon, and G. R. Luckhurst, *Mol. Phys.*, 1975, **30**, 1913.

⁴⁰ F. Poldy, M. Dvornitzky, and C. Taupin, *J. Phys. (Paris)*, 1975, **36**, Cl-27.

⁴¹ N. Boden, Y. K. Levine, D. Lightowlers, and R. T. Squires, *Chem. Phys. Letters*, 1975, **31**, 511; *ibid.*, 1975, **34**, 63.

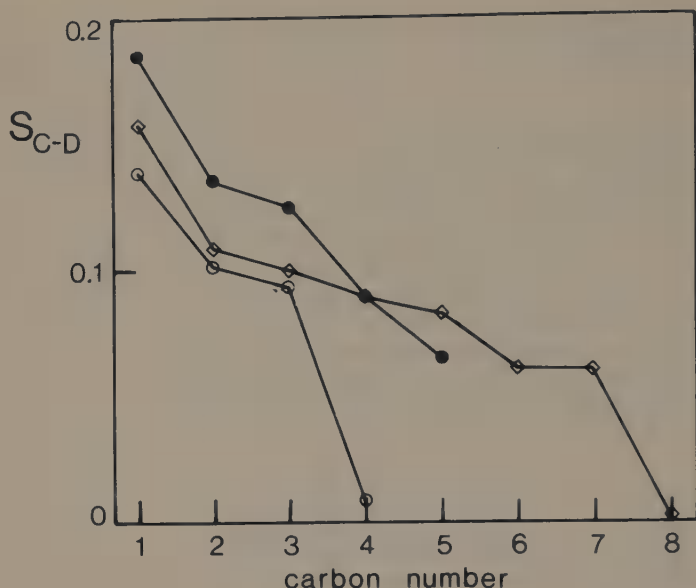


Figure 1 The order parameters S_{C-D} for the alkyl-chain segments in the mesogens 4-cyano-4'-n-pentylbiphenyl (●), terephthalylidene-bis(4-n-butylaniline) (○), and 4-n-butyloxybenzylidene-4'-n-octylaniline (◇).

where M_2 is the second moment between pairs of strongly coupled protons. For example, in an alkyl chain, the methylene protons are strongly coupled, and it is the interactions between protons in different methylene groups which contribute to M_2 . This second moment reflects the chain statistics, but the extraction of detailed information concerning the orientational order of the chain is clearly a difficult task. However, qualitative information is available from such experiments. For example, the echo amplitude for the nematic mesophase of even members of the series of 4,4'-di-n-alkyloxyazoxybenzenes is found to follow a single decay whereas the decay for the odd members can only be represented by a sum of two decays. This observation is taken to imply a discontinuous flexibility gradient for the odd members of the series; although this information is potentially valuable, experiments with simpler systems, in which protons are replaced by deuterons, are required to prove this conclusion.

Cholesterics.—The characteristic feature of the cholesteric mesophase is the helical arrangement of the director. Since the pitch of the helix is large compared with the range of the intermolecular potential responsible for the angular correlation, the helical structure should not influence the magnitude of the order parameters. The constituent molecules of most cholesterogens contain a steroidal residue and are devoid of the aromatic groups found in most nematogens. It is likely therefore that the anisotropic forces responsible for the orientational order in the phases are quite different and that this difference would be reflected in the order parameter \bar{P}_2 .

However, the apparently important problem of determining \bar{P}_2 for steroidal cholesterogens appears to have been neglected. There do not seem to be any measurements of \bar{P}_2 for the pure phase even though the birefringence has been determined.⁴² The only other measurements are for the ordering matrix of aromatic solutes dissolved in a compensated mixture of steroidal cholesterogens.⁴³

Smectic A.—Experimental studies of the smectic A phase were much stimulated by the Kobayashi-McMillan theory.⁸ One intriguing prediction of the theory is that the nematic-smectic A transition should become second-order when it occurs at or below a certain reduced temperature. If the theory is restricted to a purely anisotropic intermolecular potential, as in the Maier-Saupe theory, then this tricritical point is shown to occur when T_{S-N}/T_{N-I} equals 0.85. However, the results of various experiments suggest that this estimate is too low. For example, the order parameter of a spin probe dissolved in 4'-n-octyloxy-4-cyanobiphenyl hardly changes at the nematic-smectic A transition, which would therefore appear to be essentially second-order.⁴⁴ Since the transition occurs at a reduced temperature of 0.96, the theoretical prediction of 0.85 or less is clearly in serious error. A more refined test of the theory would be to vary the reduced temperature for the nematic-smectic A transition in order to locate the tricritical point exactly, and two ingenious experiments have been devised to accomplish this aim. In the first study the transition temperatures T_{S-N} and T_{N-I} for the mesogen 4-cyanobenzylidene-4'-n-nonylaniline were varied by increasing the pressure.⁴⁵ The two transitions have different pressure coefficients, and it was possible to decrease the reduced nematic-smectic A transition temperature while monitoring the order parameter with n.m.r. The discontinuity in \bar{P}_2 was found to vanish when the reduced transition temperature was 0.92, corresponding to a pressure of 2.89 kbar. The transition temperature T_{S-N} was varied in the second investigation by changing the composition of a binary mixture of 4-n-octyloxybenzylidene-4'-n-propylaniline and its ethoxy-homologue.⁴⁶ The order of the transition was determined from the enthalpy of transition after due correction for the contribution from pretransitional effects. The tricritical point was then identified at a reduced temperature of 0.96. These high values of the reduced nematic-smectic A transition temperature can be explained if the scalar contribution to the intermolecular potential is included. The observed values of T_{S-N}/T_{N-I} would then appear to indicate that this scalar term tends to dominate the potential.

Smectic C.—The smectic C phase differs from the A phase because the constituent molecules prefer to be tilted away from the normal layer. Consequently any molecular theory of the smectic C phase must start from a pairwise potential which constrains the molecules to be inclined to the intermolecular vector in the minimum energy configuration. This contrasts with the situation in a nematic or smectic A, where the minimum in the intermolecular potential occurs when the molecules are orthogonal to the vector. McMillan forces the molecules to tilt by the addition of

⁴² M. Evans, R. Moutron, and A. H. Price, *J.C.S. Faraday II*, 1975, **71**, 1854.

⁴³ E. Sackmann, P. Krebs, H. U. Rega, J. Voss, and H. Möhwald, *Mol. Cryst. Liquid Cryst.*, 1973, **24**, 283.

⁴⁴ G. R. Luckhurst and R. Poupko, *Mol. Phys.*, 1975, **29**, 1293.

⁴⁵ T. J. McKee and J. R. McColl, *Phys. Rev. Letters*, 1975, **34**, 1076.

⁴⁶ D. L. Johnson, C. Maze, E. Oppenheim, and R. Reynolds, *Phys. Rev. Letters*, 1975, **34**, 1143.

electric dipoles which are not parallel to the molecular long axis.⁴⁷ He then considers a particularly simple system of a layer of particles with this dipole-dipole interaction and, using the molecular field approximations, discovers a second-order transition from smectic A to a tilted smectic C phase. The rotational motion about the long axis is predicted to be quenched in the smectic C phase, but as yet there is no experimental evidence for such quenching. Indeed many experiments suggest that the rotational motion in the C phase is as unhindered as in the preceding smectic A phase.⁴⁸ Wulf has proposed that it is the interactions between the alkyl chains which are responsible for the tilt in the smectic C phase because the chains are, of necessity, not parallel to the molecular long axis.⁴⁹ The chains are assumed to be rigid entities and so the problem of chain statistics is avoided; their interaction is represented by an empirical term in the intermolecular potential. This is then treated in a manner analogous to that in the Kobayashi-McMillan theory of the smectic A phase. The theory successfully predicts a second-order phase transition between the smectic A and C phases. Unlike the smectic A phase, a smectic C is predicted to be biaxial, and the extent of the biaxiality is related to the tilt angle. In fact the deviation from cylindrical symmetry is predicted to be large, and some evidence for this can be gleaned from a careful analysis of n.m.r. spectra of smectic C phases.⁵⁰

3 Molecular Dynamics

The molecular structure of most mesogens is relatively complex, and so there are a wide variety of motions which a molecule may execute. These include translation, rotation, vibration, and internal rotation; the situation is further complicated by the possibility of coupling between these various modes. However, the motions are invariably assumed to be independent, and so we shall discuss them separately.

Translational Diffusion.—The macroscopic anisotropy of a liquid crystal demands that the translation motion be described by a second-rank tensor \mathbf{D} rather than a scalar, as in normal liquids. For uniaxial systems such as a nematic or smectic A mesophase the diffusion tensor has cylindrical symmetry whereas for a smectic C it should be biaxial although the departure from cylindrical symmetry appears to be negligible for terephthalidene-bis(4-n-butylaniline).⁵¹ Of the several techniques available for the determination of \mathbf{D} , probably the most reliable involves direct observation of the motion in an aligned mesophase. For example, Yun and Fredrickson⁵² monitored the diffusion of ¹⁴C-labelled 4,4'-dimethoxyazoxybenzene at 122 °C and found $D_{\parallel} = 4.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, with a ratio of D_{\parallel}/D_{\perp} equal to 1.25. These results clearly demonstrate the relative ease of diffusion parallel, rather than perpendicular, to the director, although the difference is not as large as anticipated. Two other ingenious methods have been devised to monitor mass migration of a probe molecule in a mesophase; in one experiment the probe is a dye, and so its progress may be observed directly.⁵³ In the other the probe is optically active;⁵⁴ this

⁴⁷ W. L. McMillan, *Phys. Rev. (A)*, 1973, **8**, 1921; R. J. Meyer and W. L. McMillan, *ibid.*, 1974, **9**, 899.

⁴⁸ Z. Luz, R. C. Hewitt, and S. Meiboom, *J. Chem. Phys.*, 1974, **61**, 1758.

⁴⁹ A. Wulf, *Phys. Rev. (A)*, 1975, **11**, 365.

⁵⁰ A. Wulf, *J. Chem. Phys.*, 1975, **63**, 1564.

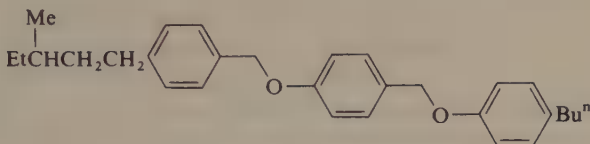
⁵¹ R. Blinc, M. Burger, M. Luzar, J. Pirš, I. Zupančič, and S. Žumur, *Phys. Rev. Letters*, 1974, **33**, 1192.

⁵² C. K. Yun and A. G. Fredrickson, *Mol. Cryst. Liquid Cryst.*, 1970, **12**, 73.

⁵³ F. Rondelez, *Solid State Comm.*, 1974, **14**, 815.

⁵⁴ H. Hakemi and M. M. Labes, *J. Chem. Phys.*, 1974, **61**, 4020.

converts the nematic into a cholesteric phase with a pitch related to the probe concentration. The magnitude of the pitch is readily gauged from the distance between the Grandjean lines, which gives the required time dependence of the concentration. The technique has been applied to a racemic mixture of (1), using one of the optical isomers as a probe,⁵⁵ so removing the objection that the results are not



(1)

directly relevant to the behaviour of the pure nematic phase. Here the enhanced molecular anisotropy results in a greater anisotropy in D ; thus D_{\parallel}/D_{\perp} ranges from 2.25 at 45 °C to 1.70 at 86 °C, while D_{\parallel} goes from $0.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ to $4.10 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for the same change in temperature.

N.m.r. spectroscopy may also be employed to determine the diffusion tensor by observing the influence of either a static or a pulsed gradient in the applied magnetic field on the form of the spin echo. The technique is difficult to apply to liquid crystals because of their complex spectra, caused by the dipolar splittings, although this difficulty has been circumvented in a number of ways. For example, the structure may be removed by using a multiple-pulse experiment in conjunction with partial deuteration; this procedure has been employed for 4-methoxybenzylidene-4'-n-butylaniline, where D_{\parallel}/D_{\perp} is found to be 1.4 at 25 °C, with D_{\parallel} equal to $6.9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.⁵⁶ The smectic C and A phases of terephthalidene-bis(4-n-butylaniline) have been studied with the same technique,⁵¹ and in the A phase D_{\parallel} is $14 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ while D_{\parallel}/D_{\perp} is 0.3. This demonstrates the ease of motion within the smectic layers in contrast to movement across the layers; again the difference is not as large as might have been anticipated. An alternative procedure to spin decoupling is to align the mesophase with the director at the so-called magic angle ($\cos^{-1} 1/\sqrt{3}$) for then the dipolar splitting vanishes and the spectrum collapses to a single line. Krüger *et al.*⁵⁷ have employed this trick to study translational diffusion in the smectic A and B phases of 4-n-dodecanoylbenzylidene-4'-aminoazobenzene. At the start of the smectic A, D_{\parallel}/D_{\perp} is only 0.6, but this decreases to 0.2 at the transition to the smectic B phase, where the anisotropy in D increases still further.

In principle, incoherent quasi-elastic scattering of neutrons from a liquid crystal can also be used to determine the translational diffusion tensor. However, the major difficulty, and possibly the strength, of this technique is that all kinds of molecular motion can contribute to the scattering. Indeed, many of the earlier measurements of D using neutron scattering are now known to be in error because the scattering vector Q employed in these experiments was so large that there was rotational broadening of the quasi-elastic peak.⁵⁸ It seems that the broadening comes entirely

⁵⁵ H. Hakemi and M. M. Labes, *J. Chem. Phys.*, 1975, **63**, 3708.

⁵⁶ I. Zupančič, J. Pirš, M. Luzar, R. Blinc, and J. W. Doane, *Solid State Comm.*, 1974, **15**, 227.

⁵⁷ G. J. Krüger, J. Spiesecke, and R. Weiss, *Phys. Letters (A)*, 1975, **51**, 295.

⁵⁸ J. Töpler, B. Alefeld, and T. Springer, *Mol. Cryst. Liquid Cryst.*, 1974, **26**, 297.

from translational motion only if the scattering vector is less than 0.3 \AA^{-1} ; under these conditions the width of the peak, $\Delta\omega_{\frac{1}{2}}$, is:

$$\Delta\omega_{\frac{1}{2}} = D_{\parallel} \cos^2 \theta + D_{\perp} \sin^2 \theta \quad (5)$$

where θ is the angle between the director and \mathbf{Q} .⁵⁹ The diffusion tensor determined for 4,4'-dimethoxyazoxybenzene, for low \mathbf{Q} values, is found to be in good agreement with that determined from tracer experiments. Similar studies have also been reported for 4-n-pentyl-4'-cyanobiphenyl using material with and without the alkyl chain completely deuteriated.⁶⁰ Since the scattering cross-section of deuterium is far less than that for a proton, it is possible to see if the chain motions contribute to the broadening. In fact the linewidth was the same for both samples, and so the broadening may be ascribed entirely to translational motion. The ratio D_{\parallel}/D_{\perp} , determined from the slopes of a plot of $\Delta\omega_{\frac{1}{2}}$ versus Q^2 , was found to be 1.3, which is close to the value for 4,4'-dimethoxyazoxybenzene. The nematogen 4-methoxybenzylidene-4'-cyanoaniline was also studied and, at 112°C , the ratio D_{\parallel}/D_{\perp} was determined to be 2.2. The relatively large difference between these values was taken as further evidence for some sort of association in 4-n-pentyl-4'-cyanobiphenyl.

Despite the considerable effort on the part of experimentalists to determine the translational diffusion tensor for nematics and other liquid crystals, there are remarkably few theoretical models to rationalize their results. One of the earliest attempts to develop a theory was made by Franklin,⁶¹ who modified the Kirkwood theory to allow for the anisotropy in the bulk viscosity of the nematic. Of course, this is an over-simplification, because in the Leslie formulation of the hydrodynamics of nematics there are five viscosity coefficients. Accordingly, Franklin⁶² has modified the original theory to take account of all these coefficients, and claims to find good agreement with the experimental temperature dependence of \mathbf{D} for 4,4'-dimethoxyazoxybenzene. Although it is helpful to have a relationship between the translational diffusion tensor and the various Leslie viscosity coefficients, a theory involving the molecular interactions might be more illuminating. Any such molecular theory must start with the autocorrelation function of the momentum \mathbf{p} , since the scalar diffusion constant is:

$$D = (kT/m\overline{p^2}) \int_0^\infty \overline{\mathbf{p}(0) \cdot \mathbf{p}(t)} dt \quad (6)$$

This approach has been adopted by Chu and Moroi,⁶³ although they only expand the correlation function for small times and then evaluate $\overline{p^2}$ and $\overline{\dot{p}^2}$ by invoking the molecular-field approximation. The theory appears to work reasonably well, although the assignment of various parameters occurring in the theory is not clear. A more reliable route to an understanding of the molecular factors determining \mathbf{D} should be provided by the powerful computer-simulation technique of molecular dynamics. One calculation is available for highly anisotropic particles interacting

⁵⁹ K. Rościszewski, *Acta Phys. Polon. (A)*, 1972, **41**, 549.

⁶⁰ A. J. Leadbetter, F. P. Temme, A. Heidemann, and W. S. Howells, *Chem. Phys. Letters*, 1975, **34**, 363.

⁶¹ W. Franklin, *Mol. Cryst. Liquid Cryst.*, 1971, **14**, 227.

⁶² W. Franklin, *Phys. Rev. (A)*, 1975, **11**, 2156.

⁶³ K. S. Chu and D. S. Moroi, *J. Phys. (Paris)*, 1975, **36**, C1-99.

with a continuous but strongly repulsive potential.²¹ However, the orientational order in this system of ellipsoids, with the major axis three and a half times the minor axis, was found to be much larger than that in a real nematic. Nonetheless, the translational diffusional tensor can be scaled, to allow for this high order, according to the common (but suspect) rule:

$$D_{\parallel}/D_{\perp} = \{D_{\parallel}^0(2\bar{P}_2 + 1) + 2D_{\perp}^0(1 - \bar{P}_2)\} / \{D_{\parallel}^0(1 - \bar{P}_2) + D_{\perp}^0(2 + \bar{P}_2)\} \quad (7)$$

where the superscript indicates the diffusion tensor for the completely aligned mesophase. Then the ratio D_{\parallel}/D_{\perp} , for an order parameter \bar{P}_2 of 0.56, is calculated to be 3.35, which is considerably higher than the values determined experimentally. There are two possible explanations for this major discrepancy between theory and experiment. One is the difficulty of knowing whether the system has reached thermodynamic equilibrium, because with highly anisotropic potentials it is possible for the system to become isolated in such metastable regions of configurational phase space. Alternatively, the purely repulsive anisotropic interaction may not be appropriate for real liquid crystals.

Rotation.—The molecular reorientation in a liquid crystal must be highly anisotropic, for, while rotation about the long axis is essentially unhindered, the motion of the long axis is constrained by the long-range orientational order. Nordio and his colleagues have developed a theory of rotational diffusion to describe these motions by extending the Debye theory to allow for the torques experienced by a molecule as a consequence of the orientational order.⁶⁴ The theory therefore relates the various rotational correlation times to the parameters in the orientational pseudopotential as well as to the components of the rotational diffusion tensor. However, the theory does not attempt to describe those factors which determine this tensor, and, as we shall see, these have yet to be assigned. The strong-collision model has also been applied to the evaluation of various rotational correlation functions involving liquid crystals; however, its only merit would appear to be its mathematical simplicity, for it is unable to relate the collisional correlation times to the order in the mesophase.²⁶

Dielectric relaxation provides a valuable technique for investigating molecular reorientation in liquid crystals, and has been applied to a variety of systems. Of course, the permittivity is now a second-rank tensor, and for most liquid crystals it possesses cylindrical symmetry. The component parallel to the director normally shows a low-frequency dispersion, associated with long-axis reorientation, as well as a high-frequency dispersion coming from rotation about the long axis. The low-frequency dispersion can normally be fitted to a single Debye relaxation⁶⁵ or a narrow Fuoss-Kirkwood distribution,⁶⁶ and the relaxation time obtained is identified with the correlation time for rotation of the long axis. For example, the low-frequency dispersion for 4-n-pentyl-4'-cyanobiphenyl can be explained in terms of a single relaxation time which decreases from 8.5×10^{-8} s at 14 °C to 2.7×10^{-8} s at 28 °C.⁶⁵ Similarly, recent measurements for certain 4,4'-di-n-alkoxyazoxybenzenes can be interpreted with a single relaxation time.⁶⁷ The temperature dependence of

⁶⁴ P. L. Nordio and P. Busolin, *J. Chem. Phys.*, 1971, **55**, 5485; P. L. Nordio, G. Rigatti, and U. Segre, *ibid.*, 1972, **56**, 2117.

⁶⁵ P. G. Cummins, D. A. Dunmer, and D. A. Laidler, *Mol. Cryst. Liquid Cryst.*, 1975, **30**, 109.

⁶⁶ V. K. Agarwal and A. H. Price, *J.C.S. Faraday II*, 1974, **70**, 188.

⁶⁷ A. Mircea-Roussel and F. Rondelez, *J. Chem. Phys.*, 1975, **63**, 2311.

the rotational correlation times for this series was analysed with the aid of a simple Arrhenius plot, and the resulting activation energies were employed to support the idea of significant pretransitional effects for those members of the series which possess a smectic C phase following the nematic. However, considerable caution must be exercised when applying such a simple approach to the analysis of the temperature dependence of the correlation time, because two quite different factors contribute to this time. The first is the long-range orientational order while the second is the rotational diffusion tensor. By employing Nordio's theory, this first contribution may be removed from the correlation time to leave the diffusion tensor. For many normal liquids this tensor is proportional to the bulk viscosity, and so there is now some effort to find which, if any, of the Leslie viscosity coefficients may be involved for a mesophase. It has been suggested that the twist viscosity coefficient may be important,⁶⁸ but the determination of the rotational correlation time in the nematic and smectic A phases of 4-cyanobenzylidene-4'-n-octyloxyaniline seems to rule out this possibility.⁶⁹ Thus the correlation time is continuous through the second-order nematic-smectic A transition whereas the twist viscosity coefficient diverges at the transition.

Reorientation about the long axis in a mesophase has not received as much attention as motion of the long axis, probably because the dispersion in the permittivity occurs in an experimentally difficult frequency range. In addition, this motion is not significantly affected by the long-range order that is characteristic of a liquid crystal. However, Evans *et al.* have studied this motion for cholesteryl oleyl carbonate in the isotropic, cholesteric, and smectic phases.⁴² They find that the correlation time is continuous at the isotropic-cholesteric transition but increases discontinuously when the smectic phase is formed. The far-i.r. spectra of the cholesteric and isotropic phases were also recorded; a broad absorption centred at *ca.* 75 cm⁻¹ was detected for both phases. By analogy with similar studies of 4-methoxybenzylidene-4'-n-butylaniline⁷⁰ this Poley-like absorption has been attributed to a librational motion of the rigid part of cholesteryl oleyl carbonate. These particular measurements probe the local structure of the system, and it would appear that this does not suffer any major changes on going from the isotropic to the cholesteric mesophase.

Of course, the major difficulty of studying molecular rotation by dielectric relaxation is knowing the exact relationship between the frequency-dependent permittivity and the dipole-moment autocorrelation function. This problem is particularly severe for liquid crystals because both the permittivity ϵ and the correlation function $\Phi(t)$ are second-rank tensors. However, linear-response theory has been employed in an attempt to allow for this anisotropy, and the following expression is obtained for the permittivity parallel to the director:

$$\frac{[\epsilon_{\parallel}(\omega) - \epsilon_{\parallel}(\infty)][\epsilon_{\parallel}(\omega) - n_{\parallel}(\omega)\{\epsilon_{\parallel}(\omega) - \epsilon_{\parallel}(\infty)\}]\epsilon_{\parallel}(0)}{[\epsilon_{\parallel}(0) - \epsilon_{\parallel}(\infty)][\epsilon_{\parallel}(0) - n_{\parallel}(0)\{\epsilon_{\parallel}(0) - \epsilon_{\parallel}(\infty)\}]\epsilon_{\parallel}(\omega)} = \int_0^{\infty} -\dot{\Phi}_{\parallel}(t) \exp(-i\omega t) dt \quad (8)$$

where $n(\omega)$ is a frequency-dependent depolarization tensor.⁷¹ The autocorrelation

⁶⁸ F. Rondelez and A. Mircea-Roussel, *Mol. Cryst. Liquid Cryst.*, 1974, **28**, 173.

⁶⁹ Y. Galerne, *Compt. rend.*, 1974, **278**, B, 347.

⁷⁰ M. Evans, M. Davies, and I. Larkin, *J.C.S. Faraday II*, 1973, **69**, 1011.

⁷¹ G. R. Luckhurst and C. Zannoni, *Proc. Roy. Soc.*, 1975, **A343**, 389.

function $\Phi(t)$ is defined in terms of the dipole moment of an ellipsoidal cavity embedded in the mesophase. Consequently the problem of relating this to the single-particle autocorrelation function remains, unless correlations between dipole moments in different molecules are ignored. Nonetheless, this theory is an improvement over the relationships implicitly adopted for $\epsilon(\omega)$, but in view of its complexity it remains to be seen if experimentalists consider that their data merit such an analysis.

There are far fewer theoretical problems in obtaining rotational correlation times from the line broadening in electron resonance, although this dynamic information relates to the motion of the spin probe and so, unless the probe is carefully chosen, may not reflect the behaviour of the pure mesophase. The theory governing the linewidths caused by the rotational modulation of the g and hyperfine tensors is reasonably well established for doublet-state spin probes.²⁶ It has recently been extended to triplet-state species where the dominant interaction is the zero-field splitting.²⁷ The macroscopic anisotropy of a mesophase results in an angular dependence of the linewidths, and this should be exploited to maximize the information available from line-broadening studies. These techniques have been employed to study the rotational motion of the spin probe (3-spiro-[2'-*N*-oxyl-3',3'-dimethyloxazolidine])-5 α -cholestane in the smectic A phase of 3-*N*-(4'-ethoxybenzylideneamino)-6-*n*-butylpyridine.²⁶ Using the diffusion model, the ratio D_{\parallel}/D_{\perp} for the components of the rotational diffusion tensor was found to be about 50 for an order parameter \bar{P}_2 of 0.89. This ratio is extremely large, and contrasts with a value of three predicted by a purely hydrodynamic model; departure from this prediction is taken to indicate essentially unhindered rotation about the long molecular axis. The same spin probe has also been employed to study the nematogen Merck Phase IV;²⁵ in this mesophase the order parameter \bar{P}_2 for the spin probe is only 0.62, and this may account for the reduction of D_{\parallel}/D_{\perp} to 35. Most experimental and theoretical investigations of line broadening in e.s.r. spectra have been confined to the fast-motion limit, partly because the spectral analysis is far simpler in this regime. The theory has been extended to the slow-motion limit and employed to analyse the line broadening in the spectrum of perdeuteriated 2,2,6,6-tetramethyl-4-piperidone-1-oxyl dissolved in the nematic mesophase of Merck Phase V.⁷² Because the spin probe is not cylindrically symmetric, the diffusion model developed by Nordio and his colleagues⁶⁴ for symmetric-top molecules was modified for asymmetric rotors. This complicates the spectral analysis, which is also inhibited by the low degree of order found for the spin probe. However, a detailed analysis is possible, and it is found that parameters obtained in the fast-motion limit cannot be used to predict their values at lower temperatures. This discrepancy can be removed by replacing the Debye-like spectral densities:

$$j(\omega) = \tau / (1 + \omega^2 \tau^2) \quad (9)$$

by the semi-empirical expression:

$$j(\omega) = \tau / (1 + \epsilon \omega^2 \tau^2) \quad (10)$$

The magnitude of ϵ is rationalized in terms of coupling of the molecular reorientation to other degrees of freedom of the spin probe's environment.

⁷² C. F. Polnaszek and J. H. Freed, *J. Phys. Chem.*, 1975, **79**, 2283.

There have been few studies of the rotational motion in liquid crystals by incoherent quasi-elastic neutron scattering, possibly because the exact theory necessary to interpret the scattering is still being developed.^{60,73,74} The central problem is the evaluation of the intermediate scattering function:

$$I_{\text{inc}}(\mathbf{Q}, t) = \exp \{-i\mathbf{Q} \cdot \mathbf{r}(0)\} \exp \{i\mathbf{Q} \cdot \mathbf{r}(t)\} \quad (11)$$

where \mathbf{r} is the position vector of the scattering centre. Provided the various motions are uncorrelated, this scattering function may be written as a product of scattering functions, and for rotation:

$$I_{\text{inc}}^{\text{rot}}(\mathbf{Q}, t) = \exp \{-i\mathbf{Q} \cdot \mathbf{a}(0)\} \exp \{i\mathbf{Q} \cdot \mathbf{a}(t)\} \quad (12)$$

where \mathbf{a} is the position vector of the scatterer with respect to the centre of rotation. Unlike the situation in magnetic resonance, it is difficult to evaluate this correlation function except for very special situations. For example, if the long molecular axis is fixed and the molecule undergoes rotational diffusion about this axis, the correlation function can be evaluated as a series expansion.⁷⁴ A Fourier transform in time then gives the so-called scattering law for rotation as:

$$S_{\text{inc}}^{\text{rot}}(\mathbf{Q}, \omega) = J_0^2(Qa \sin \theta) \delta(\omega) + \frac{2}{\pi} \sum_{n=1}^{\infty} J_n^2(Qa \sin \theta) \frac{D_r n^2}{(D_r n^2)^2 + \omega^2} \quad (13)$$

where J_n is an n^{th} -order Bessel function of the first kind and D_r is the rotational diffusion constant. The angle between \mathbf{Q} and the long molecular axis is denoted by θ . When θ is $\pi/2$ the width of the quasi-elastic peak is found to pass through a maximum at Qa equal to about 3.9. Similar results are found for other models describing reorientation about the long axis.⁷⁴

The assumptions employed in this derivation are likely to be realistic for a smectic H phase or a solid where the long molecular axes are completely ordered. Indeed, such notions have been employed to study motion in the smectic H phase of terephthalidene-bis(4-n-butylaniline) and to show the absence of any correlation between the short molecular axes.⁷⁵ The same mesogen has been studied in the solid phase, using material with deuteriated chains; apparently the scattering is caused by chain motion, and an analysis in terms of a jump-diffusion model gives a correlation time of *ca.* 10^{-12} s.⁷⁶ However, in a nematic phase and certain smectic phases the orientational order is not high, but, provided the rotation of the long axis can be ignored, then the scattering law can be obtained by taking the appropriate average over θ . Such averaging complicates the resultant scattering function even in the simplifying situations with \mathbf{Q} either parallel or perpendicular to the director. There is, however, a more serious problem with this approach, for it is by no means certain that the motion of the long axis can be ignored when evaluating the scattering law. Indeed, although e.s.r. studies confirm the expected anisotropy in the rotational diffusion tensor, this is not sufficiently large as to justify the neglect of long-axis motion. It would appear that we must await further theoretical developments before incoherent quasi-elastic neutron scattering can be employed to study rotational motion in a nematic.

⁷³ K. Rościszewski, *Physica*, 1974, **75**, 268.

⁷⁴ A. J. Dianoux, F. Volino, and H. Hervet, *Mol. Phys.*, 1975, **30**, 1181.

⁷⁵ H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, *Phys. Rev. Letters*, 1975, **34**, 451.

⁷⁶ F. Volino, A. J. Dianoux, R. E. Lechner, and H. Hervet, *J. Phys. (Paris)*, 1975, **36**, C1-89.

Internal Rotations. There have been relatively few investigations of the dynamics of internal motion for molecules within a liquid-crystal mesophase. However, the situation might well get better, because the improvement in spectrometer design has removed many of the experimental difficulties in measuring nuclear spin relaxation times. In addition, preliminary observations suggest that deuterium relaxation times for the alkyl chains of the mesogen are dominated by internal rotations. At present, neutron scattering has been employed to study alkyl-chain motions in 4-methoxybenzylidene-4'-n-butylaniline.⁷⁷ The correlation time governing the motion is said to be 3×10^{-12} s, but we have seen that the analysis of neutron-scattering experiments is fraught with difficulties. Ultrasonic absorption would appear to provide an alternative technique.⁷⁸ Close to the order-disorder transition, the attenuation is governed by critical fluctuations, but at lower temperatures the absorption by internal modes is important. Thus for the nematogen Merck Phase V a single absorption at 2×10^7 Hz is observed and attributed to *trans-gauche* isomerization in the alkyl chains.

PART II: Continuum Behaviour

4 Continuum Theory for Nematics and Cholesterics

Curvature Elasticity.—A nematic specimen is never a perfect single crystal; the axis with respect to which the molecules are preferentially aligned never points in exactly the same direction throughout. Even if it is not deliberately distorted by strains imposed at its surfaces, or by the application of electric or magnetic fields, it may still be riddled by disclinations; and even if the disclinations are eliminated by careful annealing, distortions are bound to arise through thermal agitation alone.

Let us describe the local axis of alignment by a unit vector \mathbf{n} , known as the director, bearing in mind that, since the molecules in nematics never seem to distinguish up from down, the states described by \mathbf{n} and $-\mathbf{n}$ must be treated as equivalent. Now suppose we choose a cartesian co-ordinate system (the director frame) such that \mathbf{n} lies along the z -axis at the origin. To specify the degree of distortion around the origin we need to specify the local derivatives of \mathbf{n} such as $\partial n_x / \partial x$, and the first objective of the continuum theory of nematics is to generate an expression for the free-energy density in powers of these. Much the same problem arises in the theory of elasticity of solids. There we describe the local strain by specifying the derivatives such as $\partial X / \partial x$ of a displacement vector with components (X , Y , Z), and any reader who is familiar with the subject should be able to convince himself that if the solid is uniaxial, if its symmetry axis coincides at the origin with the z -axis, and if the distortion is such that Z is everywhere zero, then the free-energy density is given in terms of the usual elastic constants by:

$$f = f_0 + \frac{1}{2} c_{11} \left[\left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} \right)^2 \right] + \frac{1}{2} c_{44} \left[\left(\frac{\partial X}{\partial z} \right)^2 + \left(\frac{\partial Y}{\partial z} \right)^2 \right] + \frac{1}{2} c_{66} \left[\left(\frac{\partial X}{\partial y} - \frac{\partial Y}{\partial x} \right)^2 \right] - 2c_{66} \left[\left(\frac{\partial X}{\partial x} \frac{\partial Y}{\partial y} - \frac{\partial X}{\partial y} \frac{\partial Y}{\partial x} \right) \right] \quad (14)$$

⁷⁷ J. A. Janik, J. M. Janik, K. Otnes, and K. Rościszewski, *Physica*, 1974, **77**, 514.

⁷⁸ S. Nagai, P. Martinoty, S. Candau, and R. Zana, *Mol. Cryst. Liquid Cryst.*, 1975, **31**, 243.

The answer for nematics is almost identical, if we replace $\partial X/\partial x$ by $\partial n_x/\partial x$ and so on; the first-order derivatives of n_z necessarily vanish, because \mathbf{n} is a unit vector which can vary in direction but not in length, and that is why there was no need to include in equation (14) any terms involving Z . It seems that in the nematic case the coefficients of the fourth and fifth terms in the formula equivalent to equation (14) are not necessarily related, but this is scarcely relevant because the fifth term can in any case be discarded. We discard it because

$$\frac{\partial n_x}{\partial x} \frac{\partial n_y}{\partial y} - \frac{\partial n_x}{\partial y} \frac{\partial n_y}{\partial x} = \frac{\partial}{\partial x} \left(n_x \frac{\partial n_y}{\partial y} \right) - \frac{\partial}{\partial y} \left(n_x \frac{\partial n_y}{\partial x} \right)$$

from which it follows that an integral of the fourth term over any sheet that is everywhere normal to \mathbf{n} is completely specified by the boundary conditions at the edge of that sheet. A term in the free energy that depends only on boundary conditions can have no influence on the direction of \mathbf{n} somewhere in the interior*.

The starting point for the continuum theory of nematics is therefore the formula:

$$f = f_0 + \frac{1}{2} K_1 \left[\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y} \right)^2 \right] + \frac{1}{2} K_2 \left[\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x} \right)^2 \right] + \frac{1}{2} K_3 \left[\left(\frac{\partial n_x}{\partial z} \right)^2 + \left(\frac{\partial n_y}{\partial z} \right)^2 \right] \quad (15)$$

in the director frame, or, in any frame of reference:

$$f = f_0 + \frac{1}{2} K_1 (\text{div } \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot \text{curl } \mathbf{n})^2 + \frac{1}{2} K_3 (\mathbf{n} \times \text{curl } \mathbf{n})^2 \quad (16)$$

The three Frank stiffness constants which feature in this formula are, in practice, very much smaller than the elastic constants of a typical solid, which is why nematics distort so easily. It is also the reason, incidentally, why we may safely assume that, unless the distortion is very marked indeed (e.g. in the core of a disclination), it has no effect on the degree to which the molecules are aligned, i.e. on the local value of \bar{P}_2 , and hence on other properties – such as the stiffness constants themselves – which, in principle, may depend upon the degree of alignment. In the materials so far investigated the stiffness constants lie in the range 10^{-7} – 10^{-6} dyn; they decrease on heating, and $K_3 \geq K_1 > K_2$.† K_1 is known as the splay constant, K_2 as the twist constant, and K_3 as the bend constant.

Left to itself, a nematic specimen minimizes its total free energy by letting its director relax to the least distorted configuration that is consistent with the boundary conditions. In principle, however, we may prevent the director from relaxing by applying a suitable torque to each molecule from outside. The torque required may readily be calculated from equation (16) by application of the principle of virtual work, and hence we may calculate the equal and opposite torque which is exerted on the molecules internally, by the distortion of the director. The general expression is too complicated to be worth writing out here.

Cholesteric liquid crystals closely resemble nematics, but because they are composed of optically active molecules they like to adopt a configuration in which the

* Nehring and Saupe¹³⁹ have shown that terms in the free energy of nematics depending on second-order derivatives such as $\partial^2 n_y / \partial y \partial z$, introduced by Oseen but lost sight of by most later authors, may in practice be discarded for much the same reason.

† Some theories suggest that K_1 and K_3 should become equal in the limit $\bar{P}_2 \rightarrow 0$.

director twists in a spiral fashion about an axis perpendicular to itself. For cholesterics the appropriate generalization of equation (16) is:

$$f = f_0 + \frac{1}{2}K_1(\text{div } \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \cdot \text{curl } \mathbf{n} \pm q_0)^2 + \frac{1}{2}K_3(\mathbf{n} \times \text{curl } \mathbf{n})^2 \quad (17)$$

where $2\pi/q_0$ is the pitch of spiral that the cholesteric likes best. The sign to be attached to q_0 in (17) depends upon whether the spiral is right- or left-handed.

Viscosity.—Naturally enough, extra stresses and torques develop in a nematic as soon as it begins to flow. Let us treat it as Newtonian and assume the stresses to be related in a linear fashion to the gradients of the flow velocity $\mathbf{V} = (u, v, w)$. If the director is rotating they may also be affected by the speed of its rotation, but for the moment we shall suppose \mathbf{n} to be fixed despite the flow. Symmetry considerations then allow us to write down equations for the shear stress components which, once more in the director frame, take the following form*:

$$t_{zx} = \eta_1 \frac{\partial w}{\partial x} + \eta_4 \frac{\partial u}{\partial z} \quad (18)$$

$$t_{xz} = \eta_4 \frac{\partial w}{\partial x} + \eta_2 \frac{\partial u}{\partial z} \quad (19)$$

$$t_{xy} = t_{yx} = \eta_3 \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \quad (20)$$

For an ordinary isotropic fluid the four coefficients introduced above would all be equal to the conventional shear viscosity η .

In principle, we can measure η_1 , η_2 , and η_3 by using a simple viscometer in which the flow is planar and only one component of the velocity gradient tensor is non-zero. Suppose, for example, that we fix \mathbf{n} (e.g. with the aid of a large magnetic field) so that it lies along the direction of the flow and the aligned molecules are made to slide over one another in a lengthwise fashion, then we shall measure η_1 . If we fix \mathbf{n} so that it lies perpendicular to the flow planes and the molecules are made to slide over one another end to end, then we shall measure η_2 . In the third principal configuration, with \mathbf{n} fixed in the flow planes, but perpendicular to \mathbf{V} , we shall measure η_3 . It generally turns out in practice (for recent measurements on 4-methoxybenzylidene-4'-n-butylaniline see ref. 79) that $\eta_2 > \eta_3 \geq \eta_1$, which is perhaps hardly surprising. Incidentally, the difference between η_1 and η_3 means that, if we do the experiment with \mathbf{n} in the flow planes but at some angle to \mathbf{V} , other than 0 or $\pi/2$, then the tangential stress experienced by the viscometer must have a component perpendicular to \mathbf{V} . Furthermore, if a nematic fluid is forced to undergo Poiseuille flow between flat plates while the director is held at an angle, a transverse pressure gradient should develop. The latter effect, reminiscent of the Hall effect perhaps, has recently been demonstrated by Pieranski and Guyon.⁸⁰

⁷⁹ J. W. Summerford, J. R. Boyd, and B. A. Lowry, *J. Appl. Phys.*, 1975, **46**, 970.

⁸⁰ P. Pieranski and E. Guyon, *Phys. Letters (A)*, 1974, **49**, 237.

* The reader conversant with elasticity theory may again find it helpful to explore the analogy of a uniaxial solid, to persuade himself that equations (18)–(20) are correct. In elasticity theory the coefficients relating t_{zx} to $\partial X/\partial z$ and t_{xz} to $\partial Z/\partial x$ are necessarily identical, as can readily be proved by appealing to the law of conservation of energy. It can be proved by the methods of irreversible thermodynamics that the η_4 which occurs in (18) is necessarily identical to the η_4 which occurs in (19).

The importance of η_4 is apparent when we come to consider viscous torques. Given the shear stresses described by equations (18) and (19), it follows that a nematic fluid undergoing shear flow experiences a torque per unit volume, the component of which, about the y -axis, say, is given in the director frame by:

$$G_y = t_{xz} - t_{zx} = (\eta_4 - \eta_1) \frac{\partial w}{\partial x} + (\eta_2 - \eta_4) \frac{\partial u}{\partial z} \quad (21)$$

For an ordinary isotropic fluid this evidently vanishes. It need not do so for a nematic fluid because any amount of torque can be absorbed, as it were, by whatever external agency is used to fix the director. Let us now decompose the fluid motion about the y -axis into a solid-body rotation with angular velocity ω_y and a pure shear component ξ_y ; this means writing:

$$\frac{\partial w}{\partial x} = \xi_y - \omega_y, \quad \frac{\partial u}{\partial z} = \xi_y + \omega_y \quad (22)$$

Then we may write:

$$G_y = \gamma_1 \omega_y - \gamma_2 \xi_y \quad (23)$$

where:

$$\gamma_1 = \eta_1 + \eta_2 - 2\eta_4, \quad \gamma_2 = \eta_1 - \eta_2 \quad (24)$$

At this stage let us admit the possibility that the director is not fixed, but is rotating about the y -axis with angular velocity say Ω_y . The appropriate generalization of equation (23) is clearly:

$$G_y = \gamma_1 (\omega_y - \Omega_y) - \gamma_2 \xi_y \quad (25)$$

which ensures that, in the absence of shear, and when the whole specimen is rotating as a solid body, director and all, the viscous torque vanishes.

The coefficient η_4 therefore plays a role in determining the so-called torque coefficient or twist viscosity γ_1 . This is of particular importance in experiments where, for example, a nematic sample is allowed to oscillate as a solid body in a magnetic field strong enough to hold \mathbf{n} fixed^{81,82} or alternatively where the nematic is stationary and the magnetic field is changed in direction. It is γ_1 which determines the decay rate of the oscillations in one case and the rate at which \mathbf{n} relaxes to its new equilibrium configuration in the other.

The twist viscosity has an additional significance for cholesterics because it controls the rate of *permeation*. Suppose we have a cholesteric specimen in which the axis of the cholesteric spiral points along the y -axis in the director frame, and suppose that the fluid is in uniform motion in this direction with velocity V , while for some reason the phase of the cholesteric spiral is unable to change. The fact that \mathbf{n} is fixed in space means that in each element of fluid it is rotating with angular velocity $\Omega_y = Vq_0$. This implies a viscous torque per unit volume $G_y = -\gamma_1 Vq_0$, and to provide the energy dissipated against this torque there must be a pressure gradient. A simple calculation shows that

$$V = -(\gamma_1 q_0^2)^{-1} (dp/dy) = -\lambda_p (dp/dy) \quad (26)$$

⁸¹ P. J. Flanders, *Mol. Cryst. Liquid Cryst.*, 1974, **29**, 19.

⁸² S. Meiboom and R. C. Hewitt, *Phys. Rev. Letters*, 1975, **34**, 1146.

The smallness of the permeation coefficient λ_p , defined by equation (26) may explain, as Helfrich originally pointed out, the anomalously high apparent viscosities reported for cholesterics by some of the early experimenters who measured rates of flow through tubes.

So far we have four independent viscosity coefficients for a nematic, viz. η_1 , η_2 , η_3 , and η_4 or γ_1 . The need for a fifth becomes apparent when we have occasion to consider the normal stress components in the director frame. If we regard the nematic as incompressible and therefore ignore the complications associated with bulk viscosity, equations for the normal stresses may be written thus:

$$t_{xx} = -p + 2\eta_3 \frac{\partial u}{\partial x}; \quad t_{yy} = -p + 2\eta_3 \frac{\partial v}{\partial y}; \quad t_{zz} = -p + 2\eta_5 \frac{\partial w}{\partial z} \quad (27)$$

where p is the pressure that would exist in the absence of velocity gradients.

It may be added that many authors prefer to use a set of Leslie coefficients α_1 to α_5 , rather than the η 's defined above. The relationships between the α 's and the η 's are set out by Stephen and Straley.⁵

5 Applications of Continuum Theory

The ability of the theory, which has been summarized above, to explain a vast range of intriguing phenomena was amply demonstrated in the years before 1973, and little that is essentially new has emerged since then except in relation to flow instabilities and to the effects of smectic ordering. These matters will be dealt with in Sections 6 and 7, respectively. In the present section a survey of the pre-1973 work on nematics and cholesterics will be conducted, and a number of elegant experiments that have been carried out since 1973 by way of extension of this work will be described. The reader should bear in mind that many of these experiments lead in the end to values for the stiffness and viscosity coefficients of the material under investigation. To improve our stock of information about these coefficients is a worthwhile objective by itself for any investigator, since the information will no doubt be needed shortly for comparison with microscopic theories.

Fredericksz Transitions.—While liquid crystals still cost £1 per gram or more, there is some incentive to devise experiments that can be done on small samples, and in fact many of the experiments to be described in this section were done on thin films contained between two glass (or similar) slides. In a thin film the boundary conditions for \mathbf{n} are naturally of overwhelming importance. The boundary conditions depend upon the treatment of the glass. If it has been carefully rubbed over a sheet of paper, always in the same direction, then where the liquid crystal makes contact with the glass \mathbf{n} is obliged to lie parallel to the surface and in the rubbing direction. The same condition can be achieved more easily and reproducibly by evaporating onto the glass at a slanting angle a thin film of, say, silicon monoxide. If the glass has been treated with suitable surfactants then \mathbf{n} is obliged to lie perpendicular to the surface. Thus we can obtain between two glass slides a film of nematic that is almost a single crystal, aligned either in a *planar* (\mathbf{n} parallel) or a *homeotropic* (\mathbf{n} perpendicular) sense.

Now suppose that we subject such a film to a magnetic or electric* field. Because the susceptibility of a nematic is anisotropic, the field adds a term of the form: $-\frac{1}{2}\chi_{\parallel}(\mathbf{n} \cdot \mathbf{H})^2 - \frac{1}{2}\chi_{\perp}(\mathbf{n} \times \mathbf{H})^2$ to the free-energy density in the magnetic case and something similar in the electric case. Now the difference $(\chi_{\parallel} - \chi_{\perp})$, denoted by χ_a , is almost invariably positive for nematics. Hence, in the presence of a magnetic field, a nematic can lower its free-energy density by an amount $\frac{1}{2}\chi_a H^2$ by allowing \mathbf{n} to point along \mathbf{H} rather than perpendicular to it, and for intermediate orientations the nematic experiences a magnetic torque. This means that, if we start with the planar nematic field shown in Figure 2, with \mathbf{n} oriented initially along the x -axis, and apply a

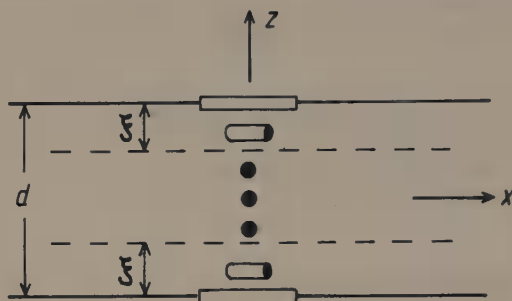


Figure 2 Cross-section through a planar nematic film above the Freedericksz transition induced by the application of a magnetic field along the y -axis. Cylinders are drawn to indicate schematically the local orientation of the director.

magnetic field along the y -axis, the single-crystal configuration becomes unstable at a certain critical field H_c . Above this critical field it pays for \mathbf{n} in the interior of the film to swing round into the y -direction, even though this introduces some twist distortion in the neighbourhood of the surfaces. If the twist is confined to two thin layers of thickness ξ , small compared with the thickness of the film d , then the free energy per unit area should be something like:

$$F_0 - \frac{1}{2}\chi_a H^2(d - \xi) + K_2 \xi (\pi/2\xi)^2$$

where F_0 is the free energy per unit area in the untwisted state. From this expression it is easy to see that, above the transition, we should expect:

$$\xi \approx (K_2/\chi_a H^2)^{\frac{1}{2}} \quad (28)$$

in equilibrium, and that:

$$H_c \approx (K_2/\chi_a d^2)^{\frac{1}{2}} \quad (29)$$

In a film of thickness $20 \mu\text{m}$, the critical field might be *ca.* 10 kG.

This type of transition is known as a Freedericksz transition. The reader must be left to imagine for himself the variety of different geometries in which similar transitions can be studied, using planar or homeotropic films, and parallel or perpendicular fields, and to consult de Gennes's book² concerning the possibilities that exist for cholesterics, where a large enough magnetic field is capable of unwinding the spiral. In many of these geometries, of course, the distortion of \mathbf{n} near

* A.c. electric fields with frequencies in the kHz range are to be preferred in this context. Low-frequency or d.c. fields may trigger off the electrohydrodynamic instabilities discussed in Section 6.

the surface of the film involves splay or bend rather than twist, and H_c therefore depends upon K_1 or K_3 rather than K_2 . When an electric field is employed rather than a magnetic one, it is of course the anisotropy of the dielectric constant which matters, and it should be noted that this quantity ($\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$) is sometimes positive and sometimes negative.

Most Freedericksz transitions are easy to detect (e.g. with a polarizing microscope) but the one illustrated in Figure 2 is not readily spotted,⁸³ which is why K_2 is less often determined than K_1 and K_3 . Recently, however, methods have been devised involving tilted fields,⁸⁴ or crossed magnetic and electric fields applied simultaneously,⁸⁵ whereby all three stiffness constants can be found.

Other recent work⁸⁶ concerns the dynamics of the transition, which is of technical importance in relation to display devices. Under this heading may be included an experiment where the transition is stimulated by application of a continuously rotating magnetic field,⁸⁷ from which γ_1 can be deduced.

Finally, something very like a Freedericksz transition can be brought about in planar films of some nematics by twisting one surface with respect to the other in the absence of any field. When the twist exceeds a critical value that may be as high as 6π , \blacksquare in the interior of the film suddenly tilts into the perpendicular configuration, and the twist can then relax. A careful study of this effect⁸⁸ suggests that, very close to the nematic-isotropic transition, $2K_2 \rightarrow (K_2 + K_3)$ in these materials.

Disclinations.—Disclinations are line defects, somewhat resembling the edge and screw dislocations that occur in solid lattices. In a nematic film that has recently been subjected to some mechanical disturbance they are normally to be seen in great abundance, and they are indeed the threads or *nema* which give the nematic phase its name. A dislocation is defined, of course, by its Burgers vector. The equivalent quantity for a disclination is an angle, namely the angle by which \blacksquare would appear to a Maxwell demon to rotate during a journey round the disclination and back to his starting point. The disclination may be classified by an index s , which is $\pm\frac{1}{2}$ if the angle is $\pm\pi$, ± 1 if the angle is $\pm 2\pi$, and so on. In addition we need to distinguish two principal types of disclination, depending upon whether the rotation occurs about an axis parallel to the disclination or perpendicular to it. Some authors refer to these, loosely perhaps, as screw and edge disclinations, respectively. Figure 3 may help the reader to visualize some of the disclinations that arise most frequently in practice.

It was originally thought that all disclinations had some sort of core, in which perhaps the liquid was isotropic, since the simple two-dimensional models illustrated in Figure 3 suggest singularities in $\text{div } \blacksquare$ or $\text{curl } \blacksquare$ on the axis. It is now recognized, however, that, round disclinations of integral s , \blacksquare usually tilts into the third dimension, and thereby adopts a configuration that is everywhere non-singular.⁸⁹⁻⁹¹ The nature of the core in $s = \pm\frac{1}{2}$ disclinations remains an interesting question about which very little is known.

⁸³ R. Dreher, *Z. Naturforsch.*, 1974, **29a**, 125.

⁸⁴ H. J. Deuling, M. Gabay, E. Guyon, and P. Pieranski, *J. Phys. (Paris)*, 1975, **36**, 689.

⁸⁵ H. J. Deuling, E. Guyon, and P. Pieranski, *Solid State Comm.*, 1974, **15**, 277.

⁸⁶ D. W. Berreman, *Appl. Phys. Letters*, 1974, **25**, 12.

⁸⁷ F. Brochard, L. Léger, and R. B. Meyer, *J. Phys. (Paris)*, 1975, **36**, C1-209.

⁸⁸ R. Turner and T. E. Faber, *Phys. Letters (A)*, 1974, **49**, 423.

⁸⁹ S. I. Anisimov and I. E. Dzyaloshinskii, *Soviet Phys. (J.E.T.P.)*, 1973, **36**, 774.

⁹⁰ R. Turner, *Phil. Mag.*, 1974, **30**, 13; **31**, 719.

⁹¹ C. Williams and Y. Bouligand, *J. Phys. (Paris)*, 1974, **35**, 589.

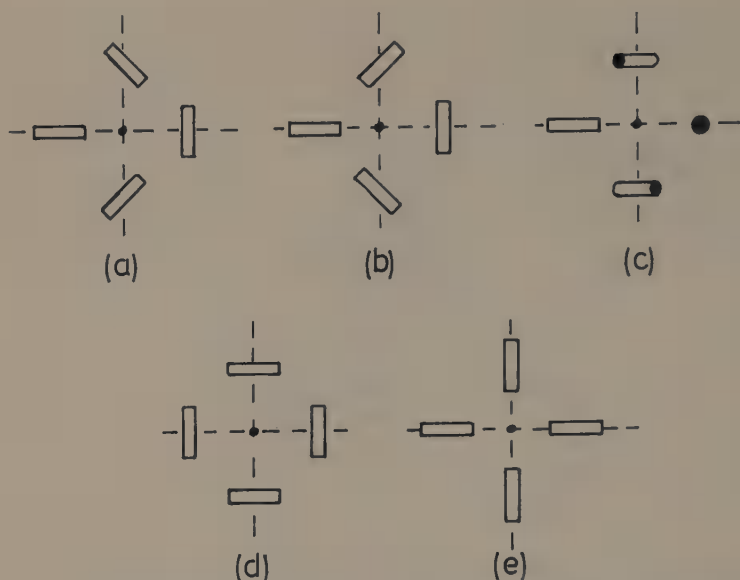


Figure 3 Orientation of the director around some common disclinations. In each case the disclination itself is perpendicular to the plane of the diagram. (a) screw, $s = +\frac{1}{2}$; (b) screw, $s = -\frac{1}{2}$; (c) edge, $s = \frac{1}{2}$; (d) screw, $s = +1$; (e) screw, $s = +1$.

Continuum theory may be used to make predictions about the line tension of disclinations, about the way they should interact with each other and with solid surfaces, and about the direction and speed at which they should move when the nematic is sheared or subjected to a magnetic field. A start has been made on the task of verifying these predictions experimentally.^{92,93}

To classify the line defects that may arise in cholesterics is a more complicated task. Because a cholesteric has a structure with layers in it, dislocations can occur as well as disclinations, similar to the dislocations in smectics that will be mentioned in Section 7. Their topology has been discussed in detail by Bouligand⁹⁴ and Rault.⁹⁵

Flow Alignment.—If a nematic specimen containing no disclinations is undergoing steady planar shear flow, as shown in Figure 4, in which direction will the director choose to set itself, boundary conditions permitting? Presumably in some direction such that the viscous torque vanishes. One such direction is along the y -axis in Figure 4, but there is another possibility, suggested by equation (24). Suppose we choose our z -axis to lie at an angle θ to the flow velocity (see Figure 4). Then clearly $\xi_y = -\omega_y$ for $\theta = 0$ and $\xi_y = +\omega_y$ for $\theta = \pi/2$. In general, $\xi_y = -\omega_y \cos 2\theta$, which means that G_y vanishes when

$$\cos 2\theta = -\gamma_1/\gamma_2 = 1 - 2(\eta_4 - \eta_1)/(\eta_2 - \eta_1) \quad (30)$$

⁹² J. A. Guerst, A. M. J. Spruijt, and C. J. Gerritsma, *Phys. Letters (A)*, 1973, **43**, 536.

⁹³ G. Malet, J. Marignan, and O. Parodi, *J. Phys. (Paris)*, 1975, **36**, L-317.

⁹⁴ Y. Bouligand, *J. Phys. (Paris)*, 1974, **35**, 215, 959.

⁹⁵ J. Rault, *Phil. Mag.*, 1974, **30**, 621.

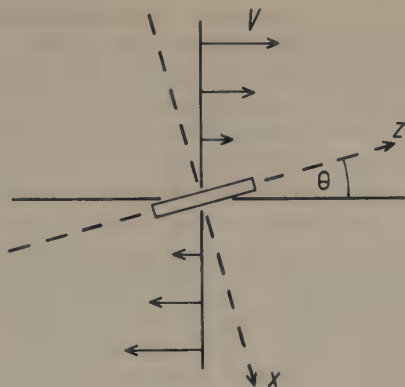


Figure 4 Stable orientation of the director in a nematic undergoing uniform planar shear flow. Arrows indicate the flow velocity.

It turns out, on closer examination, and has now been demonstrated experimentally,⁹⁶ that it is the second of these possibilities which represents the stable configuration. The experimental results are rather well described by a microscopic theory due to Forster,⁹⁷ which suggests:

$$-\gamma_1/\gamma_2 = 3\bar{P}_2/(\bar{P}_2 + \alpha) \quad (31)$$

where α depends upon the shape of the molecules. For molecules which can be treated as rigid ellipsoids with a length to breadth ratio of a/b , $\alpha = (1 + 2b^2/a^2)/(1 - b^2/a^2)$, so the theory turns out to imply that:

$$\tan \theta = b/a \text{ for perfect alignment } (\bar{P}_2 = 1)$$

$$\theta \rightarrow \pi/4 \text{ for poor alignment } (\bar{P}_2 \rightarrow 0)$$

Thus in most nematics, at most temperatures, θ is a modest angle, a typical value being in the region of 15° .

We shall discover in Section 7, however, that, in a nematic which is on the point of going smectic, η_1 may become very large, and once it becomes larger than η_4 there ceases to be any real solution for equation (30). What is thought to happen in that event is that the director adopts a non-uniform configuration, in which the angle θ changes continuously from one shear plane to the next. The viscous torque is then balanced locally by a torque due to the bend and splay in the nematic. This 'tumbling' pattern of steady flow (not to be confused with the convective patterns to be discussed in Section 6) may have been observed recently by Cladis and Torza.⁹⁸

Ultrasonic Attenuation.—A theory for the attenuation of both longitudinal and transverse sound waves in nematics has been worked out, and by comparing it with

⁹⁶ P. Pieranski and E. Guyon, *Phys. Rev. (A)*, 1974, **9**, 404.

⁹⁷ D. Forster, *Phys. Rev. Letters*, 1974, **32**, 1161.

⁹⁸ P. E. Cladis and S. Torza, *Phys. Rev. Letters*, 1975, **35**, 1283.

experimental results it is possible to obtain values for the viscosity coefficients.⁹⁹⁻¹⁰¹ The theory is not straightforward, because the shear component of the flow pattern in the sound wave is liable to cause some realignment of \mathbf{n} , quite apart from complications associated with thermal conduction and bulk viscosity. When sound is propagated along the spiral axis of a cholesteric it may affect the pitch of the spiral in a periodic fashion, and when the wavenumber of the sound wave coincides with q_0 there is a 'Brillouin zone' effect¹⁰² and a discontinuous jump in the attenuation coefficient.¹⁰³

Surface Ripples.—The ripples of short wavelength, or Rayleigh waves, which are excited thermally on the surface of any liquid and which can be studied by light-scattering techniques are of considerable interest in liquid crystals. A ripple is liable to introduce splay or bend (depending on the boundary conditions at the free surface), and potential energy may be stored in this distortion as well as in the more usual surface-tension term. For nematics the extra energy is likely to be negligible, but it could be detectable in cholesterics and smectics.^{104,105} The most recent experimental work in this field is described in ref. 106.

Rayleigh Scattering.—By Rayleigh scattering is meant the quasi-electric scattering of laser light that is such a marked feature of nematics and cholesterics – hence their milky appearance. It is not to be confused with inelastic Brillouin scattering. Both types of scattering are due to fluctuations in the body of the specimen, and in both cases the fluctuations can be described theoretically in terms of a set of periodic modes, thermally excited, and with a mean-square amplitude proportional to temperature, as required by the law of equipartition of energy. But the modes responsible for Brillouin scattering are the ordinary Debye modes of the system, *i.e.* sound waves. The modes responsible for Rayleigh scattering are distortion modes, in which the fluid remains almost stationary while it is the direction of \mathbf{n} which varies in a periodic fashion. Because nematics and cholesterics are strongly birefringent, any periodic variation in the direction of \mathbf{n} is likely to mean a periodic variation in the refractive index seen by a plane-polarized light beam passing through the specimen, and it is this that causes the strong scattering. By measuring the scattered intensity as a function of angle for various geometries one may determine the mean-square amplitude of each mode, and by analysing the frequency spectrum of the scattered beam one may determine the frequency spectrum of the modes. One of the principal achievements of continuum theory has been the detailed explanation of data obtained from experiments of this kind (for a recent example, see ref. 107).

The modes are, of course, to be labelled by a wave-vector \mathbf{q} , and for each value of \mathbf{q} there are two possible polarizations; the distortion is a mixture of splay and bend in one case, and of twist and bend in the other (becoming pure splay or pure twist when

⁹⁹ J. C. Bacri, *J. Phys. (Paris)*, 1974, **35**, 601.

¹⁰⁰ K. Miyano and J. B. Ketterson, *Phys. Rev. (A)*, 1975, **12**, 615.

¹⁰¹ S. E. Munroe, G. C. Wetsel, M. R. Woodard, and B. A. Lowry, *J. Chem. Phys.*, 1975, **63**, 5139.

¹⁰² J. D. Parsons and C. F. Hayes, *Solid State Comm.*, 1974, **15**, 429.

¹⁰³ I. Muscutariu, S. Bhattacharya, and J. B. Ketterson, *Phys. Rev. Letters*, 1975, **35**, 1584.

¹⁰⁴ J. D. Parsons and C. F. Hayes, *Phys. Rev. (A)*, 1974, **10**, 2341.

¹⁰⁵ A. Rapini, *Canad. J. Phys.*, 1975, **53**, 968.

¹⁰⁶ D. H. McQueen and V. K. Singhal, *J. Phys. (D)*, 1974, **7**, 1983.

¹⁰⁷ H. Fellner, W. Franklin, and S. Christensen, *Phys. Rev. (A)*, 1975, **11**, 1440.

\mathbf{q} is perpendicular to \mathbf{n} and pure bend when these two vectors are parallel). The mean-square amplitude predicted by the theory, expressed as the mean-square angle through which \mathbf{n} is rotated when the mode is thermally excited, is:

$$\overline{\psi^2} = kT/VKq^2 \quad (32)$$

where K is an appropriate combination of K_1 , K_2 , and K_3 . Naturally all three stiffness constants can be deduced from the scattering data, if they are not already known. The modes are heavily overdamped by viscosity, of course, the rotational inertia of the molecules being negligible in virtually every context such as this. Their frequency spectra are therefore Lorentzian, centred about $\omega = 0$ and with a width of order Kq^2/η (much less than the frequency qv_s of \mathbf{n} Debye mode of the same wavelength). Scattering experiments can therefore yield values for the viscosity coefficients as well.

Nuclear Magnetic Relaxation.—The distortion modes discussed briefly in the previous section are also relevant to the theory of the anomalous relaxation times that are observed in n.m.r. experiments on protons in nematics and cholesterics: these relaxation times, T_1 and T_2 , are generally a good deal shorter than for the same material in its isotropic phase, and they become shorter still as the magnetic field in which the experiment is done is reduced.

There may of course be a number of relaxation processes at work, but the one that is normally blamed for the anomalies just described has to do with the dipole-dipole interaction between protons attached to adjacent carbon atoms in the same molecule. As the molecule librates, and the angle between the line joining the two protons and the magnetic field changes, the strength of this interaction varies. In the isotropic phase it varies rapidly with a coherence time that may be 10^{-10} s or less, and its frequency spectrum is therefore a rather broad Lorentzian. Out of this frequency spectrum, only the components in two narrow bands centred on ω_L and $2\omega_L$ (where ω_L is the resonant Larmor frequency, always much less than 10^{10} s $^{-1}$) contribute to the spin relaxation rate $1/T_1$. The shorter the coherence time the less intensity there is in these bands and the slower the relaxation rate. We have the usual motional narrowing situation, where T_1 is long and where – because the Lorentzian spectrum has a flat top – it is independent of ω_L and therefore of the strength of field used.

The situation is different for a nematic, because the librations of the molecule are constrained. If we think first of the case of perfect alignment ($\bar{P}_2 = 1$), the only motions allowed to each molecule are rapid rotations about the local direction of \mathbf{n} and the relatively slow co-operative rocking motions which correspond to excitation of distortion modes. This was first pointed out by Pincus, who found that the rocking motions should contribute to the relaxation rate a term proportional to:

$$\frac{V}{(2\pi)^3} \int \left(\frac{k_B T}{KVq^2} \right) \frac{8\pi q^2 dq (Kq^2/\eta)}{[\omega_L^2 + (Kq^2/\eta)^2]} \quad (33)$$

[see equation (32) and the remarks that follow it]. If the upper limit to this integral may be taken as infinity, the result is proportional to ω_L^{-4} .

Later authors have tried to extend this theory to the case of imperfect alignment and have obtained a result of the form:

$$1/T_1 = A + B\bar{P}_2^2 \quad (34)$$

where the frequency-independent term A takes care of other relaxation processes. This has been fitted to some sets of experimental data with fair success, but there are serious discrepancies. Something of a controversy has therefore blown up between those who argue that a Pincus-type theory, modified perhaps by application of a cut-off to the integral in equation (33) at a finite wavenumber q_c ,¹⁰⁸ is sufficient^{109,110} and those who believe that an altogether different frequency-dependent relaxation mechanism involving diffusion of the molecules is at work.¹¹¹

To the present author it seems clear that there must be a cut-off q_c , and that its magnitude can be established by the same argument that is used to establish the cut-off in the Debye theory: one cannot have more distortion modes than there are degrees of freedom in the system. But by specifying the amplitude and phase of every mode up to this cut-off, one provides a complete description (within the framework of a continuum model) of the misalignment of the molecules, and it is quite inappropriate to suppose that there is enough order left on the microscopic scale to justify the addition of a factor \bar{P}_2^2 to the Pincus formula. A more elaborate treatment is required. It leads to formulae for $1/T_1$ and $1/T_2$ which include terms proportional to ω_L^{+1} and $\ln \omega_L$ as well as the conventional term proportional to ω_L^{-1} . It looks as though they may explain the data rather well.¹¹²

6 Dynamic Instabilities

Thermal Convection.—Readers may be familiar with the Benard convection cells which are liable to develop in an ordinary fluid when it is heated from below, with the not-unrelated cells that may develop between two coaxial cylinders rotating at different angular velocities, and with the phenomenon of turbulence in shear flow. These can all be classed as dynamic instability effects. Liquid crystals also become unstable in many circumstances, and much ingenuity has been devoted to attempts to discover just when and how they do so. Some very curious results have been established.

To take a particularly spectacular example, it is now known that a nematic layer can be set into convection by heating it from the top. In a layer a few mm thick a temperature difference between top and bottom of only one degree may be sufficient. The effect was first predicted and observed for layers with homeotropic alignment (i.e. with \blacksquare vertical) of any nematic material whose thermal conductivity is anisotropic in a positive sense (i.e. $K_{\parallel} > K_{\perp}$). The explanation for it is indicated by Figure 5(a). In this Figure, the rods which are used to indicate the local alignment of \blacksquare show that this has acquired a small tilt in the central region, initially as the result of a chance fluctuation. Because the thermal conductivity is anisotropic, the heat current in this central region is not entirely vertical; it has a component from left to right. As a

¹⁰⁸ J. W. Doane, C. E. Tarr, and M. A. Nickerson, *Phys. Rev. Letters*, 1974, **33**, 620.

¹⁰⁹ S. D. Goren, C. Korn, and S. B. Marks, *Phys. Rev. Letters*, 1975, **34**, 1212.

¹¹⁰ W. Wölfel, F. Noack, and M. Stohrer, *Z. Naturforsch.*, 1975, **30a**, 437.

¹¹¹ R. Blinc, M. Vilfan, and V. Rutar, *Solid State Comm.*, 1975, **17**, 171.

¹¹² T. E. Faber, to be published.

result, heat is being drained from the regions marked '−' in the figure and is accumulating in those marked '+'. The resultant density difference has started a circulation of the liquid, as suggested by a dotted line. The flow associated with this circulation is exerting a clockwise torque on the director and is therefore enhancing the fluctuation with which the process began.

Space does not permit further discussion of the thermal convection problem, but at least three interesting papers on the subject, describing results for cholesterics as well as nematics, have been published in the past two years.^{113–115}

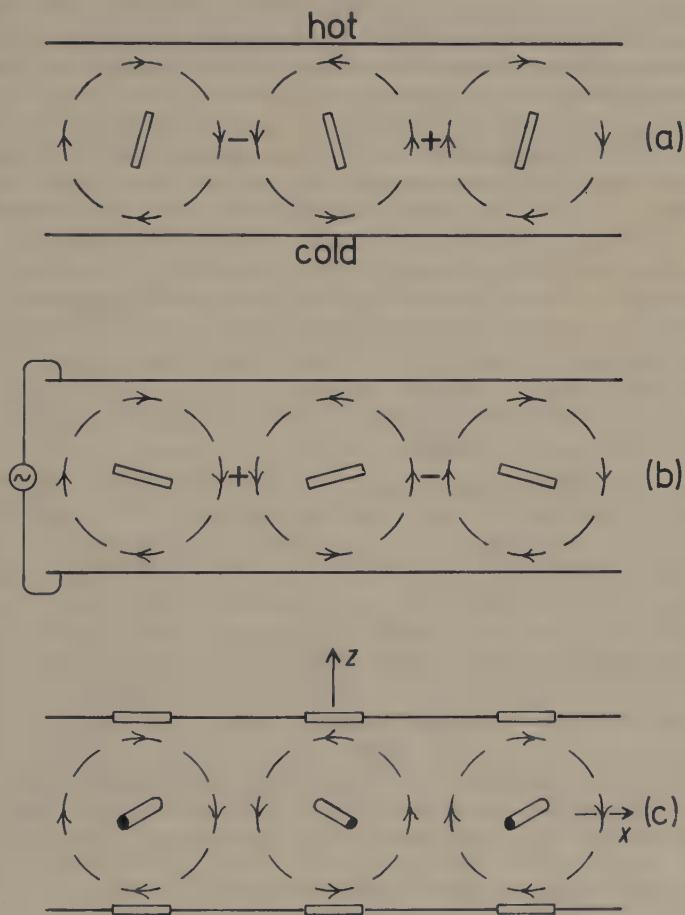


Figure 5 Convection in nematic films. (a) Thermal convection induced by heating the top of a homeotropic film; + and − indicate regions which are hot and cold, respectively. (b) EHD convection induced by an a.c. voltage across a planar film; + and − now indicate space charge in the fluid, during the half cycle when the top of the film is positive with respect to the bottom; the circulation originates from the force exerted on the space charge by the field. (c) Convection induced by uniform shear flow in a homeotropic film; the top surface of the film is moving along the y-axis into the paper. (N.B. In this instance the co-ordinate system used is not the director frame.)

Electrohydrodynamic Convection.—Rolling convective cells, of much the same appearance as the ones caused by temperature gradients, may be set up in planar nematic and cholesteric films by the application of transverse electric fields, either d.c. or audiofrequency a.c., for reasons that may be apparent from Figure 5(b). The effect is known as electrohydrodynamic or EHD convection, and the cells are known as Williams domains. The a.c. effect is easier to make sense of, because under d.c. conditions charge-injection from the electrodes may complicate the situation. With a.c., there is a threshold voltage of the order of 10 V, independent of film thickness, which increases up to some critical frequency of the order of 100 Hz. Above this frequency a different type of instability is found, where the domains are narrower and the liquid within any one domain chooses to move up and down with the frequency of the field rather than roll continuously in the same sense.

The threshold conditions for both types of EHD convection are now well understood.^{116,117} They depend not only on the anisotropy of the electrical conductivity σ but also on the sign and magnitude of ϵ_a , and the theoretical predictions have been checked for a range of materials in which $\sigma_{\parallel}/\sigma_{\perp}$ and ϵ_a take widely different values.^{118,119} Above the threshold, however, some curious and beautiful domain patterns have been observed, especially with cholesterics,^{120,121} which are still not fully understood. Nor is it known why the Williams domains in a nematic film rock slowly to and fro when the voltage is above threshold, or why the narrow domains in the high-frequency regime adopt a herringbone or chevron structure. Well above threshold, moreover, one sees a gradual transition to a generally turbid state of motion which has received little attention as yet, though it is in this turbid state that dynamic-scattering display devices work.

Convection Induced by Shear Flow.—Circulation patterns resembling Williams domains are also liable to arise when a nematic is sheared, as has recently been demonstrated in some elegant experiments by Pieranski and Guyon.^{96,122} In one of these experiments a planar nematic film between flat plates treated so as to favour alignment in the x direction is uniformly sheared by moving one plate in the y direction. Were it not for the boundary conditions, the shear would make a swing round into the favoured orientation (see Section 5) at a small angle θ to the y -axis in the yz plane, and in fact a does start to swing round in the centre of the film; it is prevented from swinging very far, however, by the twist that develops in the structure [see Figure 5(c)]. Now remember that planar shear in a nematic generates a sideways component in the shear stress, if a is aligned more or less in the flow planes but at some angle to the flow velocity other than 0 or $\pi/2$ (see Section 4). In the present instance there are bound to be shear stresses t_{xz} acting in the x -direction. Because

¹¹³ C. R. Carrigan and E. Guyon, *J. Phys. (Paris)*, 1975, **36**, L-145.

¹¹⁴ E. Dubois-Violette, *Solid State Comm.*, 1974, **14**, 767.

¹¹⁵ J. D. Parsons, *J. Phys. (Paris)*, 1975, **36**, 1363.

¹¹⁶ P. A. Penz, *Phys. Rev. (A)*, 1975, **10**, 1300.

¹¹⁷ I. W. Smith, Y. Galerne, S. T. Lagerwall, E. Dubois-Violette, and G. Durand, *J. Phys. (Paris)*, 1975, **36**, C1-237.

¹¹⁸ M. I. Barnik, L. M. Blinov, M. F. Grebenkin, S. A. Pikin, and V. G. Chigrinov, *Phys. Letters (A)*, 1975, **51**, 175.

¹¹⁹ M. Goscianski and L. Léger, *J. Phys. (Paris)*, 1975, **36**, C1-231.

¹²⁰ H. Arnould-Netillard and F. Rondelez, *Mol. Cryst. Liquid Cryst.*, 1974, **26**, 11.

¹²¹ M. de Zwart and Th. W. Lathouwers, *Phys. Letters (A)*, 1975, **55**, 41.

¹²² E. Guyon and P. Pieranski, *J. Phys. (Paris)*, 1975, **36**, C1-203.

the orientation of \mathbf{n} depends on z , these transverse stresses also vary with z , which means that a layer of the liquid of thickness Δz experiences a finite force per unit area of $(\partial t_{xz}/\partial z)\Delta z$ tending to move it sideways. The force acts in the $+y$ direction in one half of the film and in the $-y$ direction in the other half. The result is to set the nematic rolling about the direction of flow, as suggested by the dotted circles in Figure 5(c).

It is already clear that there are a great variety of flow convection patterns of this sort to be explored. It is also clear that, as the shear rate is increased, the rolling domains become unsteady, as the Williams domains do in EHD convection, and that turbulence ensues at Reynolds numbers far below those which mark the onset of turbulence in normal fluids. One may speculate that when a nematic fluid is forced at any substantial speed through a tube or past an obstacle, turbulence is inevitable, and that disclinations are created in abundance. The next challenge facing theoretical physicists or applied mathematicians in this area is surely to develop a statistical theory to describe the flow properties of \mathbf{n} bulk nematic permeated by disclinations.¹⁴¹ The next challenge for the experimentalist is to devise experiments to prove the theory inadequate!

7 Smectics

Continuum Theory of the Smectic A Phase.—Our picture of the smectic A phase in its undistorted state is of molecules arranged in regular layers of thickness t , say, each layer being perpendicular to the director \mathbf{n} — which still describes, as in nematics, the axis with respect to which the molecules are preferentially aligned. It seems intuitively likely that (a) to tilt \mathbf{n} away from the layer normal, or (b) to change t without tilting \mathbf{n} , will cost a lot in free energy, and the continuum theory of smectics in its most primitive form is based on the assumption that both these operations are forbidden. Granted this assumption, it follows that we may use the line integral $t^{-1} \int_A^B \mathbf{n} \cdot d\mathbf{l}$ to measure the number of layers that separate B from A. Since the answer must be the same whatever route between these two points we choose, it follows that the integral of $(\mathbf{n} \cdot d\mathbf{l})$ round any closed contour must vanish, and hence, by Stokes' theorem, that $\text{curl } \mathbf{n}$ must vanish. Thus [see equation (16)] a primitive smectic can sustain no twist or bend*. This is equivalent to saying that K_2 and K_3 are infinite in the smectic A phase.

We are then left with the possibility of splay distortion, and a distortion free-energy which depends only on $(\text{div } \mathbf{n})^2$. Now imagine an initially flat layer, represented by the equation $z = 0$ in the local director frame, which is bent about the origin in some way until $z = \zeta(x, y)$. Since \mathbf{n} coincides everywhere with the layer normal, it follows that in the neighbourhood of the origin $n_x = -\partial\zeta/\partial x$ and $n_y = -\partial\zeta/\partial y$, so that $\text{div } \mathbf{n} = -(\partial^2\zeta/\partial x^2 + \partial^2\zeta/\partial y^2)$. Hence we can write the free-energy density of a primitive smectic in terms of the principal radii of curvature of the layers in the region of interest, thus:

$$f = f_0 + \frac{1}{2} K_1 (R_1^{-1} + R_2^{-1})^2 \quad (35)$$

Left to themselves, therefore, the layers in a smectic prefer either to lie flat or to curve in opposite directions, like a saddle, so as to make $R_1 = -R_2$.

* If operation (a) is forbidden but not (b), then twist is forbidden but not bend.

The assumption that (a) or (b) are totally forbidden is rather a drastic one, and many situations can be envisaged where the director has no option but to tilt a little, or the layers to contract or expand, given rigid boundary conditions. It can be shown, however, that in thermal equilibrium the resultant twist or bend is necessarily confined to regions near the surfaces of the sample or to the cores of disclinations and dislocations, and that it should not infect the bulk.

It is nevertheless desirable to add to equation (35) a term to allow for the finite compressibility of the layers, of the form:

$$\frac{1}{2}B(t-t_0)^2/t_0^2$$

where t is the local layer thickness and t_0 its equilibrium value. This determines, for example, the velocity of second sound in smectics, a type of wave motion detectable by Brillouin scattering experiments in which t varies in a periodic fashion while the density stays almost constant. The theory of second sound in smectics has been discussed by Brochard.¹²³

It is believed that permeation can occur in smectics, *i.e.* that if a pressure gradient is established across the layers the liquid will flow through them at a steady rate described by equation (26). The permeation coefficient λ_p must be much smaller than in cholesterics, however, and no experiment has yet been devised to measure it. The mechanism for the process is presumably akin to the mechanism of vacancy diffusion that in principle allows a crystal which is acted on by a pressure gradient to advance at one end and retreat at the other, even when there is no motion of the lattice as a whole.

Finally, what can be said about the viscosity coefficients in the smectic A phase? The layers can slide easily enough over one another, so presumably η_2 is no larger than in the nematic phase. Likewise, η_3 should be quite small; there is little to prevent the layers from shearing in their own plane, though in this respect a smectic B phase could be very different. But the type of shear flow associated with η_1 can only take place if \mathbf{n} tilts away from the layer normal. If K_2 and K_3 are to be regarded as infinite in a smectic, then η_1 and γ_1 should be too.

Pre-Smectic Behaviour in Nematics.—It is now known that, if a nematic liquid is liable to transform into a smectic on cooling, the transition is always heralded by a marked increase in just those coefficients which we expect to be infinite in smectics, namely K_2 , K_3 , and γ_1 . A dozen papers have been published since 1973, too many to be listed here, reporting experiments in which such an increase has been observed. The subject has attracted much interest because it is one to which the Landau theory of phase transitions can be applied. This theory has already been shown to give a good account of pre-transitional effects in isotropic liquids, just above an isotropic-nematic transition..

There have in fact been two varieties of Landau theory developed for the nematic-smectic transition. One, due primarily to McMillan,¹²⁴ is of the classical mean-field type. It predicts that K_3 and γ_1 should diverge as the temperature of the transition is approached, like $(T - T^*)^{-1}$. The other, due originally to de Gennes, but carried further by Jähnig and Brochard,¹²⁵ is based on an analogy with theories

¹²³ F. Brochard, *Phys. Letters (A)*, 1974, **49**, 315.

¹²⁴ W. L. McMillan, *Phys. Rev. (A)*, 1974, **9**, 1720.

¹²⁵ F. Jähnig and F. Brochard, *J. Phys. (Paris)*, 1974, **35**, 301.

established for superconductors and liquid helium. It predicts that K_3 should diverge like $(T - T^*)^{-3}$ and γ_3 like $(T - T^*)^{-1}$. Which of them agrees best with experiment is not yet clear. It is difficult for the experimentalist to determine an exponent unambiguously from his results, because there is often a non-divergent but nevertheless temperature-dependent term in the measured quantity to be allowed for, and because he is never quite sure what to choose for T^* . An added complication is that the exponents observed experimentally seem to depend very much on purity.¹²⁶

One matter for controversy is whether the transition from nematic to smectic A is second-order or weakly first-order: if it is second-order then T^* should coincide with the transition temperature T_c , but otherwise T^* may be slightly below T_c . The material most often studied is 4-cyanobenzylidene-4'-n-octyloxyaniline and for this, at any rate, the most direct evidence available, from thermal measurements¹²⁷ and density measurements,¹²⁸ indicates a weak first-order transition. That was a surprise to some, until it was pointed out¹⁴⁰ that the twist and bend which are present due to thermal fluctuations in the nematic phase above the transition, and which must be frozen out when the material turns smectic, can play much the same role that a magnetic field does with a superconductor.

By the same token, Lubensky¹²⁹ argues that the cholesteric-smectic transition should always be first-order, because of the intrinsic twist in the cholesteric phase. Experiments on cholesteryl oleyl carbonate under pressure seem to falsify this prediction, however.^{130,131} Perhaps the argument fails because the cholesteric spiral has unwound itself before the transition is reached. Certainly the pitch has been observed, in two cases, to diverge.^{132,133}

Dislocations and Flow in Smectics.—It is much easier to persuade a smectic specimen to adopt what is virtually a single-crystal configuration than to do the same for a nematic. One has only to hold a bottle full of 4-cyanobenzylidene-4'-n-octyloxyaniline, for example, in a magnetic field and allow it to cool slowly through the nematic-smectic transition to obtain a sample in which the director is so well aligned that the milkiness which characterizes the nematic phase is almost completely removed. If the bottle is now slightly tilted the sample will be seen to flow—a little reluctantly perhaps, but enough to convince most observers that they are looking at a proper liquid. By what processes does the flow occur?

There is of course no problem in understanding the type of flow in which the smectic layers slide over one another, but suppose they lie at right angles to the direction of shear flow, as shown in Figure 6(a), what then? The work of Williams and Kléman¹³⁴ has provided most of the answers. To begin with (as the upper surface of the smectic film shown in Figure 6 is moved to the right), the layers may deform elastically, as suggested by Figure 6(b); the thickness of each layer is now necessarily

¹²⁶ P. E. Cladis, *Phys. Letters (A)*, 1974, **48**, 179.

¹²⁷ D. Dyarek, J. Baturič-Rubčić, and K. Franulović, *Phys. Rev. Letters*, 1974, **33**, 1126.

¹²⁸ S. Torza and P. E. Cladis, *Phys. Rev. Letters*, 1974, **32**, 1406.

¹²⁹ T. C. Lubensky, *J. Phys. (Paris)*, 1975, **36**, C1-151.

¹³⁰ P. H. Keyes, H. T. Weston, W. J. Lin, and W. B. Daniels, *J. Chem. Phys.*, 1975, **63**, 5006.

¹³¹ R. Shashidhar and S. Chandrasekhar, *J. Phys. (Paris)*, 1975, **36**, C1-49.

¹³² C.-C. Huang, R. S. Pindak, and J. T. Ho, *Phys. Letters (A)*, 1974, **47**, 263.

¹³³ R. S. Pindak, C.-C. Huang, and J. T. Ho, *Phys. Rev. Letters*, 1974, **32**, 43.

¹³⁴ C. E. Williams and M. Kléman, *J. Phys. (Paris)*, 1975, **36**, C1-315.

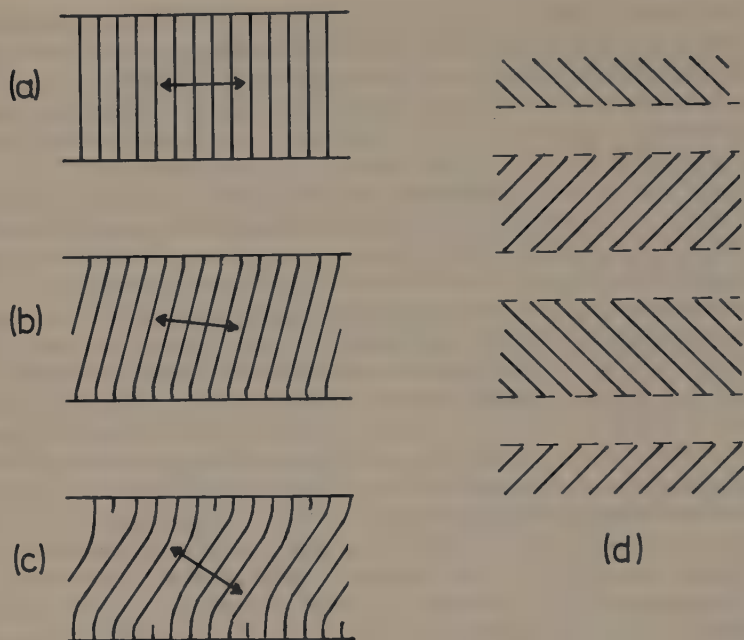


Figure 6 Layer structures in a smectic specimen; the orientation of \blacksquare is suggested by double arrows. (a) An undistorted film. (b) and (c) The same film after shear; edge dislocations have appeared in (c). (d) A bulk specimen, initially oriented as in (a), which has been stretched horizontally; between the dotted lines there are focal conic walls.

less than t_0 in the interior of the film, and \blacksquare may not everywhere be normal to the layers, so there is excess free energy stored in the layers. To release this free energy the smectic layers strive to return to t_0 in thickness, which is possible if and only if the number of layers in the specimen changes. Somehow, by a process that must involve permeation but has not yet been studied, adjacent layers must coalesce in the interior, to leave the configuration sketched in Figure 6(c). There are now edge dislocations regularly spaced along the upper and lower surfaces of the film and running at right angles to the direction of flow. Williams and Kléman have shown (see also refs. 135—137) that, once dislocations have been nucleated, it is energetically favourable for them to run together to form the type of linear defect that is illustrated in Figure 7 – equivalent to an edge dislocation of large Burgers vector, but strictly speaking a pair of disclinations ($s = \pm \frac{1}{2}$). Where the smectic layers are strongly curved, in the neighbourhood of these defects, $\text{div } \blacksquare$ is large. It therefore pays for the layers to buckle (to make $R_1 = -R_2$). The defects curve into ellipses, and a focal conic structure develops, of the sort that has been understood for many years. The layers may now be almost parallel to the shear direction in the interior, and further flow can proceed without impediment.

¹³⁵ M. Kléman, *J. Phys. (Paris)*, 1974, **35**, 595.

¹³⁶ P. S. Pershan, *J. Appl. Phys.*, 1974, **45**, 1590.

¹³⁷ P. S. Pershan and J. Prost, *J. Appl. Phys.*, 1975, **46**, 2343.



Figure 7 The layer structure around two disclinations of opposite sign, corresponding to an edge dislocation of Burgers vector $8t_0$.

Related things probably happen when a smectic single crystal is stretched along its director, a type of strain that can of course be regarded as a combination of two shear strains at 45° to the director. Very small extensions suffice to distort the layers in a periodic fashion, and one can imagine this distortion developing into the structure sketched in Figure 6(d), with focal conic walls separating each domain. What happens when a smectic is squeezed along its director is a different question. Presumably the layers must get fewer in number as they grow in area, and nucleation of edge dislocation loops must be required. The process has been discussed in a paper by members of the Orsay groups.¹³⁸ This paper, incidentally, contains some intriguing speculations about flow phenomena, dominated by permeation, which might be observable in smectic systems where nucleation of dislocations is very difficult. The speculations have yet to be confirmed experimentally.

¹³⁸ Orsay Group on Liquid Crystals, *J. Phys. (Paris)*, 1975, **36**, C1-305.

¹³⁹ J. Nehring and A. Saupe, *J. Chem. Phys.*, 1971, **54**, 337.

¹⁴⁰ B. I. Halperin and T. C. Lubensky, *Solid State Comm.*, 1974, **14**, 997.

¹⁴¹ P. G. de Gennes, *J. Phys. (Paris)*, 1974, **35**, L-217.

4 The Effect of a Magnetic Field on Chemical Reactions

By P. W. ATKINS and T. P. LAMBERT
Physical Chemistry Laboratory, South Parks Road, Oxford

1 Historical Background

The ways in which magnetic fields can affect chemical reactions have long been the subject of investigation, but only recently, with the theoretical insight given by the interpretation of chemically induced magnetic polarization,¹ has significant progress been made. The early work, which, because of the frequency of rebuttal and retraction is very hard to disentangle and even then to rely on, has been summarized in a number of reviews.²⁻⁸ More recently the subject has been analysed by Buchachenko in his book⁹ on chemically induced polarization, and in a brief, simplified article,¹⁰ but most of the work we describe has been reported only in primary journals. The magnetic field effects that have been reported (if not substantiated) range from the physiological⁷ to the purely chemical. This review ignores the former, but includes in the scope of the latter the effect of magnetic fields on the fluorescence intensity of various types of fluid sample. We shall therefore devote some attention to electrochemiluminescence phenomena, but refer elsewhere^{11,12} to reviews that assess the field in detail and relate it to its solid-state analogues.

The turmoil of the early literature is illustrated very well by the summary given in the review by Figueras Roca.⁸ For instance, in 1908, Rosenthal¹³ reported an effect of a magnetic field on the hydrolysis of starch, but this was rapidly refuted by Cegielsky¹⁴ and Heimrod.¹⁵ Selwood⁶ came to the conclusion that the catalytic activity of various ions in solutions which, according to several reports, was modified by the application of a modest field,^{16,17} was more likely to be due to the local agitation of the ions by the field than by any direct modification of their activity. More

¹ 'Chemically Induced Magnetic Polarization', ed. A. R. Lepley and G. L. Closs, Wiley, London, 1973.

² S. S. Bhatnagar and K. N. Mathur, 'Physical Principles and Applications of Magnetochemistry', Macmillan, London, 1935.

³ S. S. Bhatnagar, K. N. Mathur, and R. N. Kapur, *Phil. Mag.*, 1929, **8**, 457.

⁴ E. Miller, *Naturwiss.*, 1937, **25**, 545.

⁵ R. Delhez, *Rev. Quest. Sci.*, 1957, **18**, 176; *Bull. Soc. roy. Sci. Liège*, 1957, **27**, 161.

⁶ P. W. Selwood, *Chem. Rev.*, 1946, **38**, 41.

⁷ 'Biological Effects of Magnetic Fields', ed. M. Barnothy, Plenum, New York, 1964.

⁸ F. Figueras Roca, *Ann. Chim.*, 1967, **2**, 255.

⁹ A. L. Buchachenko, 'Chemical Polarization of Electrons and Nuclei', Nauka, Moscow, 1974.

¹⁰ P. W. Atkins, *Chem. in Britain*, 1976, **12**, 214.

¹¹ P. Avakian and R. E. Merrifield, *Mol. Cryst.*, 1968, **5**, 37.

¹² P. Avakian, *Pure Appl. Chem.*, 1974, **37**, 1.

¹³ I. Rosenthal, *Sitzber. Akad. Wiss. Berlin*, 1908, **1**, 20.

¹⁴ R. Cegielsky, *Ber. Phys. Ger.*, 1908, **15**, 566.

¹⁵ G. W. Heimrod, *Z. Elektrochem.*, 1914, **19**, 812.

¹⁶ S. N. Basmanova, *Trudy Inst. priklad. Khim. i Elektrokim. Akad. Nauk Gruz. S.S.R.*, 1962, **3**, 117.

¹⁷ A. Krause, F. Domka, and B. Marcieniec, *Monatsh.*, 1966, **97**, 99.

recently⁸ the reported magnetic inhibition of the polymerization of styrene¹⁸ appears to be contradicted,^{19,20} although a patent based on a 5% increase in the rate of polymerization of propene²¹ appears to survive. It is not in the least unlikely that commercially sensitive work continues in this field. Figueras Roca's review⁸ is an excellent source of this type of information for it concentrates on the magnetic influence on catalytic activity. Probably the most poignant summary of the early days of this type of work is provided by Mulay and Mulay,²² who make the following remark on the electrochemical studies carried out over more than a decade by Shchukarev²³ at the beginning of this century: '...after finding that the phenomena of the action of a magnetic field on chemical reactions [were] more complicated than he had originally suspected, and that they were too complex for individual observation, he decided to give up his study of the phenomena and to retract his former statements.'

The reason for the hope and scepticism of the early years lay in two rules advanced by Bhatnagar *et al.*,^{2,3} one for predicting the effect of a magnetic field on the equilibrium position of a chemical reaction, and one for predicting the effect on its rate. The former, although not phrased as such, was essentially the recognition of the possibility that the magnetic susceptibility of the reactants and the products might differ, and therefore that the standard molar reaction Gibbs function, ΔG_m^\ominus , would depend on the strength of the applied field, B . If the molar susceptibilities differ by $\Delta\chi$ this contributes $\frac{1}{2}\Delta\chi B^2$ to ΔG_m^\ominus ,²⁴ and, in principle, leads to some concomitant change in the equilibrium constant through $\Delta G_m^\ominus = -RT \ln K$. It is not difficult, however, to dismiss this effect as negligible. Even for a generous difference of susceptibilities it is hard for $\frac{1}{2}\Delta\chi B^2$ to exceed *ca.* 1 mJ mol⁻¹ in magnetic fields available in the laboratory, and the resulting shift in the equilibrium is nugatory. The early explanation of the kinetic effect (if by then it had been observed) is also untenable on the grounds of the weakness of the interaction. It was supposed^{2,3} that the field favoured some molecular orientations, thereby altering the effectiveness of collisions. What experimental results were available at the time, and which appeared to support the rules, seem to be accounted for either by agitation of the mixture or by some photochemical activity.⁸

There is one further type of magnetic activity which might play a role, but it remains to be substantiated by reliable experiments, and we shall pay no more attention to it than it receives in this paragraph. It is known that the presence of a magnetic field can influence the band structure of conductors and semiconductors (*e.g.* the de Haas-van Alphen effect), and some authors have reported changes in the work function of metals by as much as 0.1 V in quite low fields²⁵ (can that really be so?), and significant changes in their conductivities.^{26,27} If these results are depend-

¹⁸ H. Schmidt, G. Muhr, and H. Marek, *Z. Elektrochem.*, 1945, **51**, 37.

¹⁹ J. Breitenbach and F. Richter, *Monatsh.*, 1949, **80**, 315.

²⁰ S. Collins and W. A. Bryce, *J. Chem. Phys.*, 1950, **18**, 1297.

²¹ W. B. Reeves, U.S.P. 2 663 394, 1953 (*Chem. Abs.*, 1954, **48**, 4340E).

²² I. L. Mulay and L. N. Mulay, *ref.* 7, p. 146.

²³ A. N. Shchukarev, *J. Russ. Phys. Chem. Soc.*, 1915–1926.

²⁴ S. Kaneko, *J. Soc. Chem. Ind., Japan, Suppl.*, 1931, **34**, 133.

²⁵ R. Bedos, *Compt. rend.*, 1964, **259**, 1695.

²⁶ E. E. Kolosov and P. V. Sharavski, *Fiz. Doklady*, Nauchn. Konf. Leningrad, Ingh. Stroit, Inst. Leningrad, Sb., 1961, 31.

²⁷ E. Weisshaar and H. Welker, *Z. Naturforsch.*, 1958, **8a**, 681.

able they certainly suggest that heterogeneous catalytic activity might be changed by a magnetic field, and Figueras Roca⁸ has drawn attention to reports in the literature on the rate of oxidation of iron at 580 °C and the inhibition of the oxidation of formic acid in the presence of a magnetite-Cu²⁺ mixture. Nevertheless, the actual proof of magneto-catalytic activity remains extraordinarily difficult on account of the irreproducibility of samples and the elimination of extraneous complications. Although these effects are of considerable technological importance we shall devote this review to the effects that have been fully substantiated experimentally and which can be accounted for on the basis of moderately reliable theories.

Some magnetic field effects have been known and established for many years. Probably the most famous is the interconversion of ortho- and para-hydrogen: this was studied originally by Farkas and Sachsse²⁸ and explained by Wigner.²⁹ The basic idea underlying the explanation is closely related to that behind the modern theories of magnetic field effects, and a brief account will set the stage.

The interconversion of ortho- and para-hydrogen depends on the relative realignment of the two proton spins in the molecule. In ortho-hydrogen the proton spins are mutually parallel and the total nuclear spin is unity: this is the nuclear triplet state. In para-hydrogen the nuclear spins are antiparallel and the total nuclear spin is zero: this is the nuclear singlet. As a result of the requirements of the Pauli exclusion principle³⁰ only the odd rotational energy levels may be populated if the nuclear spins are arranged as the triplet (we shall call this 'triplet phased') and only the even levels if the nuclei are singlet phased. The rotational energy levels are sufficiently different in energy for the nuclear statistical effects to have significant thermodynamic consequences, and the rate of interconversion is so low that ortho- and para-hydrogen constitute two distinct species.

In order for an ortho molecule to be converted into a para molecule (or *vice versa*) the nuclear spins must be realigned. One way of doing this is to dissociate a collection of molecules, and then to allow random recombination. This is the dissociative mechanism, and is not the one expected to be influenced by a magnetic field (but see below, p. 72). Another way of bringing about relative realignment is to subject the molecule to a magnetic field that is inhomogeneous on the scale of the molecule. In that case the two protons will be in different magnetic fields and will precess at different rates. Precession at different rates means relative reorientation of the two nuclear spins, and so ortho switches into para, and *vice versa*. One way of generating a sufficiently inhomogeneous magnetic field is to allow collisions between hydrogen molecules and either paramagnetic species^{23,31-33} (ions or neutral molecules) or magnetic surfaces.³⁴ Theory suggests that the rate of interconversion should be proportional to the square of the magnetic moment of the paramagnetic species, and this accords with experiment. The interconversion process has recently been the

²⁸ L. Farkas and H. Sachsse, *Z. phys. Chem.*, 1933, **23B**, 1, 19.

²⁹ E. P. Wigner, *Z. phys. Chem.*, 1933, **23B**, 28.

³⁰ P. W. Atkins, 'Quanta: a Handbook of Concepts', Clarendon Press, Oxford, 1974.

³¹ H. Sachsse, *Z. phys. Chem.*, 1934, **24B**, 429.

³² W. K. Wilmarth and M. K. Baes, *J. Amer. Chem. Soc.*, 1953, **75**, 2237.

³³ G.-M. Schwab, J. Voitlander, and V. Penka, *Z. phys. Chem.*, 1963, **36**, 378.

³⁴ D. D. Eley and D. Shooter, *J. Catalysis*, 1963, **2**, 268.

subject of renewed attention³⁵⁻³⁷ and detailed theories of the process in the gas and liquid phases are now available. One chemical application has been to the estimation of the size of hydration spheres of ions in solution.³⁶

Many important chemical reactions involve two electron spins, either paired (as in a singlet) or parallel (as in a triplet). The significance of the ortho-para interconversion work should now be clear: local inhomogeneous magnetic fields can interchange singlet and triplet *electron* spin phasings as well as nuclear spin phasings, and can thereby affect the course of the reaction. Since the electron spins have much stronger magnetic moments than the protons, we can expect the difference in precession frequency to be greater for a given magnetic field difference. There is every hope, therefore, that the local field inhomogeneities can modify the course of reactions, and this is confirmed by experiment. The remainder of this review explores this idea for radical reactions and fluorescent processes involving excited triplet states of molecules. We shall see that the various types of spin rephasing process are the central reasons for the response of chemical reactions to magnetic fields.

2 The General Theoretical Background

Modern theories of the effects of magnetic fields^{9,38-41} are based on two effects, and both are related to the interconversion of spin multiplets. The problem can be illustrated by considering the simple case of the homolysis of a bond in the molecule $A-B$ to give two doublet radicals, 2A and 2B . We suppose first that the homolysis occurs from a singlet state of AB and that the bond cleavage occurs without alteration of the overall spin of the molecule. This means that the two spins of the bond remain antiparallel even though they are now confined to spatially separated radicals. In other words, homolysis leads to a singlet radical pair $\{^1{}^2A \cdots ^2B\}$. If the homolysis proceeds through a triplet state of AB (as it might in a photochemical cleavage), the same argument implies the formation of a radical pair in an overall triplet spin state, $\{^3{}^2A \cdots ^2B\}$. The components of the radical pair diffuse apart, but they have a significant probability of re-encountering each other. If they re-encounter they may form a bond: this is *geminate recombination* and the product is called the *cage product*. The bond will form, however, only if the radicals have singlet-phased electron spins when they re-encounter: if the electrons are triplet phased (parallel) the bond will not form and the encounter will be unproductive. If a mechanism exists for destroying the initial singlet phasing of the radical pair, it follows that the probability of geminate recombination is reduced. In that case the proportion of cage products declines relative to the *escape products*. If the magnetic field can influence the rate at which the singlet character of the radical pair is lost, it will affect the proportions of cage and escape products.

The loss of singlet phasing implies a gain in overall triplet phasing. The process by which this comes about is the same as in the ortho-para interconversion process

³⁵ S. E. Nielsen and J. P. Dahler, *J. Chem. Phys.*, 1967, **46**, 732.

³⁶ P. W. Atkins and M. J. Clugston, *Mol. Phys.*, 1974, **27**, 1619.

³⁷ E.-A. Reinsch, *Mol. Phys.*, 1974, **28**, 683.

³⁸ R. Kaptein, Thesis, Leyden, 1971.

³⁹ R. Lawler and G. T. Evans, *Ind. Chem. Belges*, 1971, **36**, 1087.

⁴⁰ R. Sagdeev, Yu. N. Molia, K. M. Salikhov, T. V. Leshina, M. A. Kamha, and S. M. Shein, *Org. Magn. Resonance*, 1973, **5**, 603.

⁴¹ A. L. Buchachenko and Sh. A. Markarian, *React. Kinetics Catalysis Letters.*, 1974, **1**, 157.

(which was for nuclei – now we deal with electrons), and is illustrated in Figure 1. The singlet state of a pair of electrons can be depicted as in Figure 1(a): we see that not only does the state consist of an α and a β spin but their relative azimuth is such that the resultant spin angular momentum is zero.³⁰ On the other hand, a triplet state of two electron spins can be constructed in three ways. One uses an equal mixture of α and β spins, but their relative azimuth is such as to give a resultant spin angular momentum of unity (actually $\sqrt{2}\hbar$), Figure 1(b). The difference between the arrangements in Figures 1(a) and 1(b) illustrates what is meant by the difference of the 'phasing' of the α and β spin orientations in the singlet and triplet states. There are two other ways of obtaining a total spin of unity. One is to use two α spins: this gives a state with $S = 1$, $M_s = +1$ (Figure 1(c)), which is denoted T_{+1} . The other uses two β spins: this gives $S = 1$, $M_s = -1$ (Figure 1(d)), a state denoted T_{-1} .

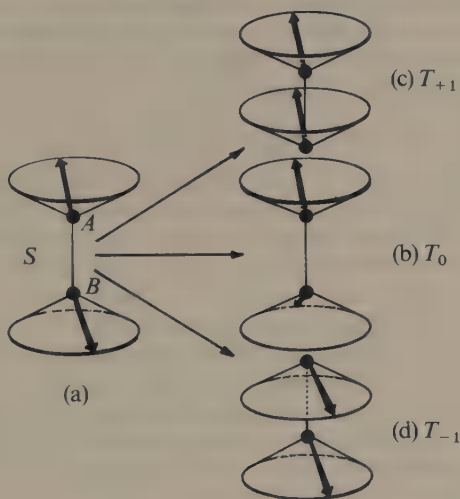


Figure 1

A singlet-phased pair of spins can be induced to switch into a triplet if their individual precession frequencies differ. For example, if the Larmor precession frequency of spin A in Figure 1(a) differs from that of spin B, they will not maintain their initial singlet phasing but will evolve into the phasing characteristic of T_0 . If the (circular) frequencies differ by $\Delta\omega$, complete conversion will occur in a time $\pi/\Delta\omega$. A difference of Larmor precession frequencies about the z -direction depends on the two spins experiencing different fields along z . It is also quite possible for the spins to experience different local fields pointing along the x - and y -directions. Such fields exert torques about their directions (about the x and y axes) and tend to twist α spins into β and β spins into α . It follows that a singlet state may have its α spin twisted into β (if the field is sufficiently different at the two electrons) and so evolve into T_{-1} , or its β spin twisted into α , which takes it into T_{+1} . In summary, therefore, we see that local magnetic fields, different at the two electrons of a radical pair, can induce singlet-triplet interconversions, and the triplet state generated (its M_s value) depends on the orientation of the local field inhomogeneity.

This qualitative discussion can be made more quantitative as follows. If the energy of spin A is determined by a term $f_A \cdot s_A$ in a Hamiltonian, and that of spin B by a term $f_B \cdot s_B$, the total Hamiltonian can be written

$$H = f_A \cdot s_A + f_B \cdot s_B = \frac{1}{2}(f_A + f_B) \cdot (s_A + s_B) + \frac{1}{2}(f_A - f_B) \cdot (s_A - s_B) \quad (1)$$

For our purposes the important term is the second. This is antisymmetric in the spins, and so it contributes to matrix elements $\langle T | H | S \rangle$ because the singlet is antisymmetric in the spins, the triplet is symmetric, and the whole matrix element must be symmetric if it is not to be zero. The term proportional to $s_A - s_B$ vanishes if $f_A = f_B$, and this is the basis of the earlier assertion that the individual Larmor precession frequencies (which are proportional to f_A and f_B) must differ if singlet-triplet transitions are to occur.

In order to identify what contributions to the Hamiltonian may induce singlet-triplet rephasing, we have to find interactions of the form $f \cdot s$ that are different for the two radicals. One candidate is the Zeeman interaction. If the g -values of the radicals are g_A and g_B their interaction with the external field B is

$$H = g_A(\mu_B/\hbar)Bs_{Az} + g_B(\mu_B/\hbar)Bs_{Bz} \quad (2)$$

and the antisymmetric part of this is proportional to $(g_A - g_B)B$. Its magnitude increases with B , and so the rate of singlet-triplet conversion should *increase* as the applied field is increased. Notice that this interaction has operators relating to only the z -direction and, in terms of the qualitative picture of the process, corresponds to a relative rephasing of the two spins around the z -direction. In other words, the g -factor differences allow S - T_0 crossing, but not S - $T_{\pm 1}$. (This restriction can be lifted in some special cases.⁴²) In a field of 1 T (10 kG), taking $g_A - g_B \sim 10^{-3}$ (which is a reasonable choice for a range of organic radicals) the time for complete rephasing is about 3×10^{-8} s. We shall return to explore the significance of this remark.

Another candidate for the spin-rephasing interaction is the hyperfine interaction of each electron with the magnetic nuclei in the radicals. The antisymmetric part of the interaction $a_A I_A \cdot s_A + a_B I_B \cdot s_B$ is

$$\begin{aligned} H_{(-)} &= \frac{1}{2}(a_A I_A - a_B I_B) \cdot (s_A - s_B) \\ &= \frac{1}{4}(a_A + a_B)(I_A - I_B) \cdot (s_A - s_B) + \frac{1}{4}(a_A - a_B)(I_A + I_B) \cdot (s_A - s_B) \end{aligned} \quad (3)$$

and so this interaction can operate even if the radicals are identical ($a_A = a_B$) but their nuclear spin orientations differ ($I_A \neq I_B$). The rate of interconversion under the influence of $H_{(-)}$ depends on the nuclear spin states of the radicals because of the involvement of nuclear spin operators in $H_{(-)}$, and this is the reason why chemical reactions are a potential technique for the separation of isotopes on the basis of their spins rather than their masses. The hyperfine Hamiltonian $H_{(-)}$ has components of magnetic field in all three directions (because the nuclear moments can take up various orientations) and so it can induce transitions between the electronic singlet and all three substates of the triplet. At first sight, however, $H_{(-)}$ does not appear to depend on the strength of an *external* magnetic field. This is indeed true, but the *effectiveness* of $H_{(-)}$ in causing S - T interconversions does depend on the applied field, and this introduces one of the most important sources of a magnetic field effect.

⁴² P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Letters*, 1973, **22**, 209.

The explanation of the role of the external field in governing the effectiveness of the perturbation $H_{(-)}$ is as follows. When a perturbation acts, its success in causing a transition depends on the ratio of its strength to the energy separating the states it is tending to mix.^{30,43} This can be illustrated explicitly by a very simple calculation. Suppose a perturbation of strength $\hbar V$ acts on a system which at $t = 0$ is known to be in a state ψ_1 ; then the probability that it will be in another state ψ_2 (the only other state available) at a later time t is

$$P(t) = (2V/U) \sin^2 \frac{1}{2} Ut \quad (4)$$

where $U^2 = \Delta^2 + 4V^2$, Δ being the separation in energy of ψ_1 and ψ_2 . If Δ is very small, $2V/U \sim 1$ and the probability oscillates between 0 and 1, the latter implying total transfer to ψ_2 . If Δ is large in the sense $V \ll \Delta$, the value of $P(t)$ does not rise above *ca.* $2V/\Delta$, which is small and implies that the perturbation is unable to induce a significant transition into the other state.

In the present case the T_0 , $T_{\pm 1}$ substates of the triplet do not lie at the same energy when a magnetic field is present, and so the efficiency with which $H_{(-)}$ can induce transitions from S to T_0 , $T_{\pm 1}$ will be different in each case. The simplest situation that arises is when the singlet and triplet lie at the same *mean* energy (which is the case if exchange interactions between the components of the radical pair are very small: this is often the case for radicals that are significantly separated in the solution, but not when they are actually in contact). In this case, and in the *absence* of an external field, the hyperfine interaction can induce transitions from S to T_0 , $T_{\pm 1}$ at about the same rate (so long as it has non-vanishing matrix elements) because the triplet substates lie at the same energy. When a field is applied, the T_{-1} substate drops to an energy $\Delta \sim g\mu_B B$ below T_0 (and therefore below S , which remains degenerate with T_0), and T_{+1} rises to an energy Δ above T_0 . Therefore, although the S - T_0 crossing may continue as before, the extent of the S - $T_{\pm 1}$ crossing is decreased by a factor of *ca.* $2V/\Delta$ (where $V \sim H_{(-)}$ in this case). Since $V \sim 0.1$ mT and $\Delta \sim 1$ T, it follows that the crossings to and from $T_{\pm 1}$ are effectively quenched in a high field.

This discussion may be summarized as follows. The proportion of cage and escape products in a radical reaction in solution depends on the rate at which the spins of the radical pair change their relative orientations. The rate of S - $T_{\pm 1}$ crossing is *decreased* on the application of a magnetic field, and in regions of high field only the S - T_0 crossing plays a significant role. All three crossings may be induced by hyperfine interactions. The S - T_0 crossing may also be induced by a g -value difference in the two radicals of the pair: the strength of this interaction is proportional to the magnetic field, and the rate of S - T_0 crossing is *increased* by a field.

Being in an overall singlet is a necessary but not a sufficient criterion for recombination: the two radicals of the pair must also be in contact (in some sense). Therefore the probability that the pair is in a singlet at a time t has to be multiplied by the probability that at that time it has a spatial conformation corresponding to bonding.³⁸⁻⁴¹ If the latter probability is denoted $G(t)$, the total recombination probability depends on the value of the integral $\int_0^\infty dt G(t)P_S(t)$, $P_S(t)$ being the probability of being in a singlet at time t . For simple three-dimensional translational diffusion $G(t) \propto t^{-\frac{1}{2}} \exp(-t/\tau)$, and the integral can be evaluated; this gives the characteristic $\tau^{\frac{1}{2}}$, and thence $(\eta/T)^{\frac{1}{2}}$ behaviour of such diffusional processes and explicit expressions have been reported in several publications.³⁸⁻⁴¹

⁴³ P. W. Atkins, 'Molecular Quantum Mechanics', Clarendon Press, Oxford, 1970.

3 Experimental Examples

Substantial experimental evidence is available^{40,41} for magnetic field effects along the lines of the theory described so far. For instance, Sagdeev *et al.*⁴⁰ have examined the dependence on a magnetic field of the proportions of cage and escape products in the liquid-phase reaction between various fluorinated benzyl chlorides and *n*-butyl-lithium. The cage product, formed from benzyl + butyl radicals, is phenylpentane, and the escape products include diphenylethane. The reaction involves a singlet precursor, and so we expect the proportion of cage products to increase as the field increases (*S-T* inhibited). The report indicates that for benzyl chloride itself the ratio of phenylpentane to diphenylethane does indeed increase, and changes from 4.7 ± 0.3 to 5.6 ± 0.5 when the applied field is changed from $50 \mu\text{T}$ (0.5 G) to 1.5 T (15 kG).

The same authors also studied the effect of temperature and solvent on the field dependence. Typical results are those relating to pentafluorobenzyl chloride and *n*-butyl-lithium. The ratio of products rose from 4.5 ± 0.5 to 6.2 ± 0.3 when the solvent was *n*-hexane at 70°C and the field was increased from $50 \mu\text{T}$ to 2.5 T (25 kG), an increase of *ca.* 37%, but it changed from 4.0 ± 0.3 to 6.1 ± 0.5 in cyclohexane at 70°C , an increase of *ca.* 54% (probably the record so far). In cyclohexane at 80°C the ratio changed from 3.7 ± 0.3 to 5.3 ± 0.5 . The magnetic field is expected to have a smaller effect at high solvent mobilities because the diffusional trajectory terminates more quickly than at low mobilities, and the rephasing effects are less pronounced because they have less time to operate.

Another class of examples is provided by the work of Gupta and Hammond,⁴⁴ who reported some intriguing results on the effect of a magnetic field on the photosensitized isomerization of piperylene (penta-1,3-diene) and stilbene (1,2-diphenylethene). They found that the photostationary state concentrations changed when a 0.9 T field was applied, and that the effect depended on the nature of both the substrate and the photosensitizer. For instance, the ratio of *trans/cis* photostationary state concentrations of the isomeric piperylenes was 1.08 (benzophenone as sensitizer), 1.13 (*m*-methoxyacetophenone), 1.08 (fluorenone), 1.16 (2-acetonaphthone), 1.07 (Michler's ketone), but 0.91 for stilbene (with benzophenone) and 0.95 (2-acetonaphthone). They pointed out a number of features of their results which would need to be accommodated by any theory. In the first place they considered that some kind of relaxation time must be involved, but that this could not be radiative decay of sensitizer triplets because the substrate concentrations are much greater than are needed to capture virtually all the excited triplets, and an effect on the sensitizer alone would be unlikely to influence the different isomers to different extents. They concluded that the explanation probably lay in the ability of the magnetic field to influence the relative rates of radiationless decay of triplet exciplexes.

An explanation of these experiments which conforms to the suggestions outlined here has been suggested.⁴⁵ It was proposed that the triplet exciplex should be regarded as having the nature of a radical ion pair. In that case the application of the magnetic field can stimulate an intersystem crossing because the two components of the exciplex have different *g*-values and therefore different precession frequencies in

⁴⁴ A. Gupta and G. S. Hammond, *J. Chem. Phys.*, 1972, **57**, 1789.

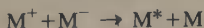
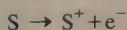
⁴⁵ P. W. Atkins, *Chem. Phys. Letters*, 1973, **18**, 355.

the same applied field. Furthermore, the rate of deactivation of the exciplex (the rate at which it is switched from triplet to singlet) will depend not only on the field strength but also on the nature of the components, as the experimental results require. The theory was expressed in simple quantitative terms,⁴⁵ and speculations about the g-value differences and the unperturbed lifetimes of the exciplex showed that it could account for the order of magnitude of the effect observed. The crucial difficulty of the theory is the magnitude of the exchange interaction between the two components of the exciplex: the theory would fail if it were much larger than the Zeeman interaction energies. Therefore, if the theory is valid, it points to a structure of the exciplex that has the two components separated by at least one solvent molecule, and possibly more.

There is clearly room for a closer analysis of the effect, and note should be taken of a brief comment⁴⁶ which suggests that triplet quenching by other radicals produced in the reaction might be another explanation. (Why that should be field dependent we shall explain in Section 4.) If, however, the orbiting model of the exciplex is tenable the development of the theoretical description could take the form of structuring the relative translational motion of the two components to take into account their mutual Coulomb interaction and some features of their exchange interaction (as has been done for some aspects of chemically induced magnetic polarization⁴⁷). Some crude potential energy surfaces are available⁴⁸ but it is most doubtful that they would be applicable to the present problem.

There has been some speculation⁴⁹ about the possibility that a high-frequency magnetic field can play a special role in influencing the rate of recombination of radicals, but there appears to be no experimental support for the suggestion. Strong static fields at low temperatures can play a role, and the recombination of hydrogen atoms has been studied.^{8,50} The authors showed that the rate of recombination was inhibited by a strong field and accounted for it on the basis that the atoms all tended to adopt β as their spin state, and the parallel electrons were unable to form bonds. A similar type of problem has been studied in connection with ion recombination processes,⁵¹⁻⁵⁴ as is described below.

When solutions of aromatic compounds, such as naphthalene and anthracene, in aliphatic solvents are exposed to high-energy radiation, excited states of molecules are produced as a result of the ion-recombination process. At high solute concentrations the main reactions are



⁴⁶ H. van Willigen, *Chem. Phys. Letters*, 1975, **33**, 540.

⁴⁷ J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, 1963, **58**, 2746.

⁴⁸ J. N. Murrell and J. Tanaka, *Mol. Phys.*, 1964, **7**, 363.

⁴⁹ S. I. Kubarev and E. A. Pshenichnov, *Chem. Phys. Letters*, 1974, **28**, 66.

⁵⁰ J. T. Jones and M. H. Johnson, *U.S. Govt. Res. Reports*, 1959, **32**, 110.

⁵¹ B. Brocklehurst, *Nature*, 1969, **221**, 921; *Chem. Phys.*, 1973, **2**, 6.

⁵² B. Brocklehurst, *Chem. Phys. Letters*, 1974, **28**, 357.

^{52a} B. Brocklehurst, *Chem. Phys. Letters*, 1974, **29**, 635.

⁵³ B. Brocklehurst, R. S. Dixon, E. M. Gardy, V. J. Lopata, M. J. Quinn, A. Singh, and F. P. Sargent, *Chem. Phys. Letters*, 1974, **28**, 361.

⁵⁴ R. S. Dixon, E. M. Gardy, V. J. Lopata, and F. P. Sargent, *Chem. Phys. Letters*, 1975, **30**, 463.

where M is the solute and S the solvent. The question that arises is the multiplicity of the excited solute molecule M^* . Both singlets and triplets may be formed, and Brocklehurst has predicted,⁵¹ that the proportion of excited states may be altered by the application of a magnetic field. The argument is as follows. If the encounters between the reacting species M^+ , M^- were random, then a triplet : singlet ratio of 3 would be expected since, of the four arrangements of the two electrons, three are triplet and one is singlet. Generally, however, the encounters are not random: the low relative permittivity of the solvent in these systems means that in only a few cases do the ions escape from their mutual Coulombic interaction, and the majority undergo geminate recombination. In such a situation, if the recombination is very fast the triplet : singlet ratio will be zero because the initial state is a singlet and there is insufficient time for significant rephasing. On the other hand, if the recombination is slow, the arguments of Section 2 lead one to expect total relaxation, and therefore approach to a triplet : singlet ratio of 3. The relative recombination and rephasing times can be discussed in a variety of ways, and the theories outlined earlier are applicable. It is helpful, for instance, to be precise about the meaning of 'slow' and 'fast' recombination times. If the time for recombination is T_R , by fast recombination is meant $T_R \ll T_1, T_2$, where T_1 and T_2 are the longitudinal and transverse electron-spin relaxation times (the former corresponding to $S-T_{\pm 1}$ rephasings and the latter to $S-T_0$). Clearly, slow recombination is when $T_R \gg T_1, T_2$. We can also distinguish an intermediate case when $T_2 \ll T_R \ll T_1$, and in this case a triplet : singlet ratio of unity is expected because of the $S-T_0$ equilibration. In summary: $T_R \ll T_1, T_2$ should give a ratio of 0; $T_1, T_2 \ll T_R$ a ratio of 3; and $T_2 \ll T_R \ll T_1$ a ratio of 1. In zero magnetic field there is no distinction between T_1 and T_2 (all three triplet levels are mutually degenerate, and degenerate with the singlet at significant separations), but in high fields the situation changes to the intermediate case. (This is the same argument as used in Section 2, but expressed differently.) Therefore we expect the triplet : singlet ratio to drop from 3 to 1 as high fields are reached.

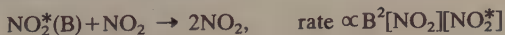
On these arguments, and with some consideration of the mobility of the substrates in the solvents, Brocklehurst⁵¹ proposed that magnetic field effects should be observable in solvents with viscosities in the range 1–10 poise. It was found⁵³ that the intensity of emission from the singlet excited state of fluorene in the solvent squalane was *enhanced* by a magnetic field, in accord with the theory. Subsequent experiments⁵⁴ examined the continuous γ -irradiation of fluorene. In squalane solutions, application of a magnetic field again significantly enhanced the emission from singlet excited fluorene. In cyclohexane solutions a magnetic field effect was also observed, but it was much less marked, as expected on the basis that cyclohexane is much less viscous than squalane. No magnetic field effect was observed when benzene was the solvent, and it is believed that excited states of fluorene are not formed by ion recombination in this case.

Brocklehurst has pointed out⁵¹ that an implicit assumption in this work is that the rates of formation of the singlet state and the triplet substates are all equal. Since Franck–Condon factors and densities of states in the singlet and triplet manifolds are unlikely to be the same, this is unlikely to be true and the pure triplet : singlet ratios of 0, 3, or 1 are unlikely to be obtained even when the conditions predict them. There is reason to hope, however, that deviations from them are likely to be small,⁵¹ and magnetic field effects should be an acceptable technique of studying the recombination process (and perhaps even of elucidating that very point).

On to the basic account of atom and ion recombination may be grafted a number of significant extra features. In the first place Brocklehurst has examined^{52,52a} the problem from the point of view of coherent rephasing of the electron spins, rather than stochastic relaxation. If the general ideas of Section 2 are borne in mind, it is easy to understand that the $S-T_0$ rephasing can be brought about by the nuclear hyperfine interaction with the two electron spins. If only one magnetic nucleus were involved, the overall state would oscillate harmonically between singlet and triplet in accord with equation (4). In the present case there are many magnetic nuclei in each species of the pair, and so the hyperfine interactions have to be summed over. This summation has the practical effect of making the singlet probability decay rather than oscillate (unless the coupling constants happen to be in simple ratios, as in perylene^{52,52a} or the magnetic nuclei are sparse) on the time-scale of interest (generally less than the Poincaré cycle time). The singlet probability is therefore predicted to fall to an average value (at slightly greater than $\frac{1}{2}$) and then to remain constant. In zero field, however, the rate of decay of the singlet under the coherent but multiple hyperfine perturbation should be greater than in the high-field case for reasons that we have already explained. A quantitative calculation is difficult because the angular momenta are orientated at random, but it has been done on the basis of a number of approximations.⁵³ The overall result is again that decay rather than oscillation occurs, but in this case the singlet population falls to a value of slightly less than $\frac{1}{2}$. The difference between the two results, one at high field the other at low, is the basis of the experimental results for the magnetic field effect on singlet recombination yields.⁵⁴

The other feature to graft on to this work is the problem of the *allowed* multiplicities when a number of ions or neutral molecules can take part in a recombination (as in a spur). On the basis that the spins do not relax or rephase there have been two conflicting sets of expressions quoted for the probability that the recombination product is a singlet (or a triplet).^{55,56} A recent analysis of the problem⁵⁷ shows it to be more complex than either of the earlier results had suggested, but the singlet recombination probabilities can be calculated for any number of participants. It is now also possible to account for spin rephasing within the spur, and the consequent effects of a magnetic field, but that work remains incomplete.

There are three examples of the effects of magnetic fields on fluorescence from the molecules in the gas phase, but as these lie at the limits of the boundaries of the present report we shall deal with them only briefly. The quenching of the fluorescence of iodine vapour^{58,59} is a result of a magnetic-field-induced dissociation of an excited state, and arises from the ability of the applied field to mix the 0_u^+ state with the unbound 0_u^- state. Similarly, the fluorescence from nitrogen(IV) oxide (NO_2) is quenched by a magnetic field.⁶⁰ In that case the field appears to operate in the collisional quenching step,



⁵⁵ J. L. Magee and J.-T. J. Huang, *J. Phys. Chem.*, 1972, **76**, 3801.

⁵⁶ B. Brocklehurst and T. Higashimura, *J. Phys. Chem.*, 1974, **78**, 309.

⁵⁷ P. W. Atkins and T. P. Lambert, in press.

⁵⁸ E. O. Degenkolb, J. I. Steinfeld, E. Wasserman, and W. Klemperer, *J. Chem. Phys.* 1969, **51**, 615.

⁵⁹ L. A. Turner, *Z. phys.*, 1930, **65**, 464.

⁶⁰ R. Solarz, S. Butler, and D. H. Levy, *J. Chem. Phys.*, 1973, **58**, 5172.

and the Lorentzian field dependence of the overall fluorescence is reproduced by the inclusion of this rate step. It has been suggested that the excited states of NO_2 are heavily perturbed by vibrational levels of the ground 2A_1 state, and magnetic mixing of the quenched state with the ground state, followed by radiationless collisional relaxation down the vibrational states of 2A_1 would account for the observations.⁶⁰ Collisions play an essential role because of the low density of states in the small molecules.

Matsuzaki and Nagakura^{61a} have reported equally interesting results on the gas-phase fluorescence from carbon disulphide. They recorded the time-dependence of the fluorescent emission from gaseous CS_2 excited by a nitrogen gas laser, and observed three band systems, of which one was due to the 1A_2 excited state. Particular attention was paid to the 1A_2 (0, 5, 0) vibronic state, and its lifetime and integrated emission intensity were measured for applied magnetic fields of up to 1.5 T. They found that both the lifetime and the integrated intensity are reduced by half when the field is *ca.* 1.3 T; this indicates that the non-radiative processes are *enhanced* by the magnetic field. They also found that the extrapolated collision-free lifetimes shortened with increasing field strength, but the collisional quenching constant remains unchanged within the limits of experimental error. At low magnetic fields (< 70 mT, 700 G) the opposite effects were observed. Once again the effects can be accounted for in terms of magnetic-field-induced mixing, the influence on a *singlet* molecule being possible because of the large spin-orbit coupling present. Very recent work^{61b} reports virtually the same behaviour for glyoxal.

4 Electrochemiluminescence

Electrochemiluminescence has turned out to be rich in examples of magnetic field effects. The processes that occur are closely related to exciton mechanisms in the solid state, and the way that these involve applied magnetic fields has received considerable attention and has been largely elucidated through the work of Merrifield,^{11,62,63} Frankevitch,⁶⁴⁻⁶⁶ and others.¹² We shall give a brief description of the solid-state processes, and then pass on to concentrate on theories and experimental results for fluids.

The theory advanced by Merrifield⁶² and Johnson and Merrifield⁶³ runs as follows. In a pair of colliding triplets there are nine possible spin states and these will occur with equal probability when the temperature is high. The rate of production of each of the nine composite states is therefore $\frac{1}{9}k_1n^2$, where n is the concentration of triplet excitons. There are two possible outcomes of the collision: one is scattering, the rate being k_{-1} , and for which there are no collision rules. The other is annihilation, with a rate that may be written $k_2S_l^2$, where $S_l = |\langle S | \psi_l \rangle|$ is the modulus of the amplitude of the singlet component in the state labelled l . It follows that the probability of annihilation from the l 'th composite exciton state is $k_2S_l^2/[k_{-1} + k_2S_l^2]$. The annihilation rate constant k is then the product of the collision rate constant and the total

⁶¹ A. Matsuzaki and S. Nagakura, (a) *Chem. Letters*, 1974, **7**, 675; (b) *Chem. Phys. Letters*, 1976, **37**, 204.

⁶² R. E. Merrifield, *J. Chem. Phys.*, 1968, **48**, 4318.

⁶³ R. C. Johnson and R. E. Merrifield, *Phys. Rev.*, 1970, **B1**, 896.

⁶⁴ B. M. Rusin and E. L. Frankevitch, *Phys. Status Solidi*, 1969, **33**, 885.

⁶⁵ E. L. Frankevitch, B. M. Romyantsev, and B. I. Lesin, *Optics and Spectroscopy*, 1974, **37**, 376.

⁶⁶ E. L. Frankevitch and B. M. Rusin, *J.E.T.P.*, 1972, **63**, 2015.

annihilation probability:

$$k = \frac{1}{9} k_1 \sum_{i=1}^9 k_2 S_i^2 / [k_{-1} + k_2 S_i^2] \quad (5)$$

The qualitative manner in which k depends on the pair spin states can be seen by considering the two limiting cases. In one limit all nine states have equal singlet character; in the other only one state is a singlet. If the annihilation rates are denoted $k(9)$ and $k(1)$, respectively, their ratio is given by the last equation, together with the requirement that S_i^2 must sum to unity, as

$$k(9)/k(1) = (k_{-1} + k_2)/(k_{-1} + \frac{1}{9}k_2) \quad (6)$$

This indicates that k is greater the more uniformly the singlet character is distributed over the nine pair states. The next problem, therefore, is the assessment of this distribution and its dependence on an applied field.

The spin-Hamiltonian for a triplet exciton consists of two terms: one is the Zeeman interaction, the other the spin-spin interaction. In the zero-field case the spin vectors of each triplet are aligned along one of the principal directions of the zero-field splitting tensor, and we speak of the T_x , T_y , and T_z states depending on the orientation of the spin with respect to these axes. The overall singlet state of two triplets can be constructed by analogy with the scalar $r^2 = x^2 + y^2 + z^2$, and is $(1/\sqrt{3})\{|T_x T_x\rangle + |T_y T_y\rangle + |T_z T_z\rangle\}$. Thus at zero field *three* of the pair states have a singlet component (by inversion of this state). As the field is turned on the zero-field states are contaminated because the Zeeman interaction provides an alternative and increasingly important quantization axis. It follows that the zero-field states begin to mix. This disperses the singlet character over more states, and so, according to the above discussion, the annihilation rate constant should *increase* in a magnetic field.

This behaviour is confined to low magnetic fields, where the spin-spin interaction, although suffering competition from the Zeeman interaction, is dominant. At high magnetic fields the Zeeman interaction is dominant, and in the limit of infinite field strength the spins are quantized exactly along its direction. Three of the joint triplet states, $|0, 0\rangle$, $|+1, -1\rangle$, $|-1, +1\rangle$ (labelled now as $|M_s, M_s'\rangle$) have a total projection of 0 and so may contribute to a singlet. Nevertheless we have to take note of the relative phasing of the $|\pm 1\rangle$ states (just as in the case of the construction of singlets and triplets out of spin- $\frac{1}{2}$ components, Figure 1) and only the *in-phase* combination $|+1, -1\rangle + |-1, +1\rangle$ can contribute to the singlet. (This can be seen explicitly by examining the vector coupling coefficients.) It follows that in the high-field case there are only two states with singlet character, and therefore a smaller annihilation rate constant than at zero field.

The general dependence of the annihilation rate constant is therefore as follows.^{62,63} At low fields it should *increase* with increasing field, pass through a maximum, and then *decrease* at high fields to a value lower than the zero-field value. Detailed analysis of the degeneracies and level crossings involved also leads to the conclusion that the high-field annihilation rate constant should be anisotropic, with minima in field directions for which the energies of the $|0, 0\rangle$ and $|\pm 1, \mp 1\rangle$ states are the same. These conclusions conform to experiment^{11,12} in the solid state and are a basis for explanations of processes in fluids.

The Johnson–Merrifield scheme has been adapted for fluid solutions by averaging the interactions over a random but stationary ensemble.⁶⁷ This is obviously a restricted view of the actual dynamical situation, and the model based on mobile species has been examined by a different technique.⁶⁸

The sequence of events treated by Atkins and Evans⁶⁸ is as follows. The triplet species diffuse from their points of generation by charge transfer from pairs of radical ions, and encounter each other at some point in the fluid medium. Since each triplet has unit spin, the total spin angular momentum of the colliding pair is 0, 1, or 2 (giving respectively an overall singlet, triplet, or quintet). The overall *singlet* pair may pass on to give fluorescence because the energy transfer step is permitted by the overall spin. This is because the energy transfer takes $^3A^* + ^3A^*$ to $^1A^* + ^1A$, and the latter can be only an overall singlet; therefore on the basis of the conservation of spin angular momentum during the energy exchange, only the $\{^3A^* + ^3A^*\}$ can give rise to $^1A^* + ^1A$. Neither the overall triplet $\{^3A^* + ^3A^*\}$ nor the overall quintet $\{^3A^* + ^3A^*\}$ can redistribute their energy to give $\{^1A^* + ^1A\}$ without violating spin conservation, and so pairs in these overall states survive the encounter.

There is, in fact, some possibility that the overall triplets and quintets do change into an overall singlet during the encounter. This can come about because of the different spin–spin dipolar interactions within each triplet (different not because the triplets are not identical, but because they are in general at different orientations to the applied field, and compete with its quantization direction). The overall quintet can switch into the singlet (the triplet–singlet switch is forbidden by symmetry for this mechanism – the spin–spin interaction is of second rank), and do so with a rate

$$\dot{P}_S(t) = \frac{4}{75}(1+c)D^2 \int_0^t dt(1+2\cos\omega t+2\cos 2\omega t)\exp(-t/\tau_R) \quad (7)$$

where $\omega = \mu_B B/\hbar$ is the Larmor frequency of the spins, D the spin–spin interaction within each triplet, and τ_R the rotational correlation time of the pair ($c = 1$ if they rotate as though stuck together; $c = 0$ if the two triplets rotate independently). The $\cos\omega t$ and $\cos 2\omega t$ terms represent the mixing of the singlet with the $M_s = \pm 1$ and $M_s = \pm 2$ states of the quintet, and we see that they contribute less to the integral at high fields (because they oscillate to positive and negative values) than at low fields. This is the effect of the removal of degeneracy already described in the earlier sections. At short times the integrand varies as $1 - \omega^2 t^2$, and so the crossing rate is inhibited by \square field. The expression for $\dot{P}_S(t)$ shows that the magnetic field effect vanishes when the triplets rotate rapidly (because the exponential term quenches the integrand if τ_R is short), the physical reason for this being that the spin–spin interaction averages to zero and ceases to compete effectively with the Zeeman interaction.

The difficulty with this mechanism is that the two colliding triplets might remain together for only a short time and the interconversion rate be so slow that only an insignificant amount switches into the singlet. What we seek is a way of permitting a long interval during which the spins are able to rephase significantly. The same requirement is needed in chemically induced magnetic polarization experiments,¹

⁶⁷ P. Avakian, R. P. Groff, R. E. Kellogg, R. E. Merrifield, and A. Suna, 'Organic Scintillators and Liquid Scintillation Counting', Academic Press, New York, 1971, 499.

⁶⁸ P. W. Atkins and G. T. Evans, *Mol. Phys.*, 1975, **29**, 921.

where the spin rephasing is allowed to take place during a diffusional trajectory which has a high probability of bringing the two components back to a re-encounter configuration. We therefore consider the following sequence of events.⁶⁸ During the initial encounter the two triplets may fluoresce if they are relatively singlet phased, but will survive as individual triplets if they are overall triplet or quintet. The encounter pair breaks up and the two triplets drift apart. Although separate, they still possess their initial phasing, but over the whole sample there is a depletion of overall singlet-phased pairs. During the translational diffusion that takes them apart the two triplets rotate. This rotation is a very efficient cause of spin relaxation on account of the strong, anisotropic spin-spin dipolar interactions within each triplet. (A few triplet spin-relaxation times in fluids have been measured⁶⁹ and found to lie in the range 2–20 ns.) The triplet spins relax independently. When, therefore, their diffusive motion brings them back into contact (or whatever a 're-encounter' involves) there is some probability that they have replenished the depleted overall singlet phasing and have regained, more or less, the thermal equilibrium distribution which had been distorted by the first encounter. If overall singlet phasing has been replenished, contact between the two species may lead to energy transfer, and thence to fluorescence. The point to emphasize at this stage is that the observed fluorescence is the totality of emission from the first encounter and the re-encounter, and the latter can contribute more effectively if spin relaxation has occurred before it takes place.

The magnetic field plays its role during the diffusional excursion. Efficient spin relaxation depends not only on the strength of the perturbative coupling (for example the anisotropy of the dipolar interactions, and in particular the spin-spin interaction) but also on the rate at which they are modulated by molecular motion (e.g. molecular rotation). Relaxation between different m_s states is most efficient when the relaxing perturbations are modulated at a rate comparable to the Larmor frequency. If the Larmor frequency is changed by an alteration of the strength of the applied field the relaxation rates will change. This is the core of the magnetic field effect on this type of fluorescent reaction: the field changes the relaxation rates, and so the extent of replenishment of the singlet is changed. This change affects the probability of energy transfer on a re-encounter, and so the fluorescence intensity depends on the applied magnetic field.

These ideas have been expressed quantitatively⁶⁸ and the following is a brief outline of the calculation. In the beginning there are two independent triplets with their spins at thermal equilibrium. The state of each is described by the thermal equilibrium density matrix σ^\ominus . Immediately before the first encounter both triplets are described in this way, and the overall state at that instant is $\rho(0_-) = \sigma^\ominus(A)\sigma^\ominus(B)$. Immediately after the collision the overall density matrix is $\rho(0_+)$. This differs from $\rho(0_-)$ in as much as some of the overall singlets have been eliminated. If \mathcal{P}_S is an operator that selects singlets, and λ is a parameter that measures the effectiveness with which an overall singlet undergoes energy transfer, we can write the final state of the triplet pair, just as it breaks up, as $\rho(0_+) = (1 - \lambda\mathcal{P}_S)\rho(0_-)$. From this point the states of the two triplets evolve independently and each one obeys the equation of motion

$$\dot{\sigma}(t) = i[\sigma(t), \mathcal{H}] + R\sigma(t) \quad (8)$$

⁶⁹ P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Letters*, 1974, **29**, 616.

\mathcal{H} is the Hamiltonian representing the effect of the applied field and R is an operator that takes relaxation into account. This equation can be solved for each triplet, using as initial conditions the joint, singlet-depleted density matrix $\rho(0_+)$. In this way it is possible to calculate the probability $P_S(t)$ that the pair of triplets is in an overall singlet at some $t > 0_+$.

In order to contribute to the fluorescence the two triplets must re-encounter each other at some stage. The probability that they do so, $G(t)$, can be evaluated on the basis of a diffusion equation, and the total contribution to the fluorescence is determined by the product of probabilities $P_S(t)G(t)$ integrated over all possible excursion times. Explicit expressions are given in the original paper,⁶⁸ and in the limit of rapid molecular motion in a strong magnetic field one finds

$$I(B)/I(0) = 1 - 0.61 \left(\frac{\lambda}{1 - \lambda} \right) D \sqrt{(\tau_R \tau)} \quad (9)$$

where D is the spin-spin interaction (zero-field splitting), τ_R the rotational correlation time, and τ the translational diffusion correlation time. This is the asymptotic behaviour, and it predicts that the intensity falls off with increasing field, as observed.

The role of stable doublet quenchers is easy to explain qualitatively, but much more difficult to deal with quantitatively. Once again the solid-state mechanisms are a guide to those operating in the fluid: if the *radiationless* quenching by the doublets is inhibited by the application of a magnetic field the fluorescence radiation will be enhanced. We shall describe the qualitative model, but not go as far as describing the actual calculation⁶⁸ (which follows much the same scheme as that outlined above).

Consider the collision of a doublet ($S = \frac{1}{2}$) and an excited triplet ($S = 1$). Their overall spin may be either doublet ($S = \frac{1}{2}$) or quartet ($S = \frac{3}{2}$). If it is the former, radiationless energy reorganization from $^2\{^3A^* + ^2Q\}$ to $^2\{^1A + ^2Q\}$ may occur without change of total spin angular momentum, but $^4\{^3A^* + ^2Q\}$ may not so reorganize. When the initial encounter pair breaks up it is depleted in overall doublet. The two components diffuse apart, but have a significant re-encounter probability. During the diffusion, spin relaxation replenishes the overall doublet, and so on re-encounter the quenching is more likely to occur than if no relaxation had occurred. The spin relaxation depends on the Larmor frequencies involved (this time of both doublet and triplet species), and so it depends on the strength of the applied field. It turns out that the significant relaxation is inhibited by the applied field, and so the radiationless quenching is also inhibited. That is just the situation necessary in order to lead to enhancement of the fluorescence, because more triplets survive doublet encounters and live long enough to meet triplet partners. These triplet encounters are also field dependent (as described earlier), but the observed increase in fluorescence indicates that the quenching responds to the magnetic field in the dominant way.

The calculational difficulty in the quantitative formulation of the model is the need to treat it as at least a three-particle collision (doublet, triplet, and another triplet). Nevertheless, the overall effect has been estimated, and the observed increase in fluorescence intensity with field strength can be accounted for.⁶⁸

There are, of course, many loose ends in both calculations, and there is room for a much more detailed analysis of the quenching sequence. Furthermore the description of the processes going on during the encounters themselves remain to be unified into a single coherent calculation rather than remaining in their present disjointed

form. When this is analysed in more detail the type of argument used by Perisamy and Santhanam⁷⁰ on the Marcus description of the electron-transfer step may play a role in the overall scheme.

The type of experimental information available can be illustrated by the following selection of papers. For instance, Faulkner and Bard⁷¹ examined the magnetic field dependence of the chemiluminescence from electron transfer reactions involving the ion-radicals of a variety of aromatic hydrocarbons. In particular they studied the reaction of the radical cation formed from *NNN'*-tetramethyl-*p*-phenylenediamine (Wursters' Blue, WB henceforth) with the anion radicals of anthracene and 9,10-diphenylanthracene (DPA). From the standard electrode potentials it is clear that the energy available from the ion-radical annihilation involving WB^+ and a hydrocarbon radical anion is insufficient to produce the hydrocarbon in its first excited singlet (such systems are called 'energy deficient'). This excited state is attainable from the reaction between DPA^+ and DPA^- (an 'energy sufficient' system). In a magnetic field the authors found that for solutions containing WB the emission intensity from the excited singlet increases with applied field (by *ca.* 20% in 0.6 T for anthracene-WB), but in the solution containing only DPA the field had no effect on the emission intensity.

Faulkner and Bard draw two conclusions from these results:⁷¹ first, that paramagnetic species are involved in at least one rate-determining step for light emission from the energy-deficient system, and that the rate of that step is field-dependent, and secondly, either that no paramagnetic species are involved in the rate-determining steps for fluorescence in the case of DPA alone, or that paramagnetic species are involved, but that behaviour is unaffected by the field. Furthermore, unless one supposes that the magnetic field can influence the diffusional characteristics (*e.g.* the diffusion constants), the rate of a diffusion-controlled reaction cannot be altered by the field in the manner observed and the rate-determining steps for the energy-deficient system studied are probably not diffusion controlled. The DPA energy-sufficient system, however, may or may not have diffusion-controlled, rate-determining steps.

The results for the energy-deficient system were rationalized by supposing that if the hydrocarbon triplet is formed in the radical annihilation step, then triplet-triplet annihilation leads to the first singlet-excited state by the energy-exchange process discussed in the earlier part of this section. In contrast the reaction involving annihilation of DPA^+ and DPA^- is believed to result in the direct formation of an excited singlet DPA molecule. The magnetic field dependence occurs as we have already described, and the increase in fluorescence intensity is compatible with the inhibition of radiationless triplet quenching by the presence of stable doublets (WB^+). It has also been pointed out in support of this mechanism⁷¹ that Parker *et al.*⁷² have provided substantial evidence to support the view that triplet-triplet annihilation is not generally a diffusion-controlled process for aromatic hydrocarbons and might occur by means of a resonance energy transfer mechanism that can operate over a great distance.

⁷⁰ N. Perisamy and K. S. V. Santhanam, *Chem. Phys. Letters*, in press.

⁷¹ L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, 1969, **91**, 209.

⁷² C. A. Parker, in 'The Triplet State', ed. A. B. Zahlan, Cambridge University Press, 1967.

This early work was followed by a series of studies on related systems. In the case of anthracene in dimethylformamide (DMF)⁷³ for example, it was observed that the fluorescence intensity decreased with increasing field and was proportional to the square of the incident excitation intensity. The intensity of delayed fluorescence under steady-state illumination is expected to obey the expression⁷²

$$I = \frac{1}{2} \phi_t k_a (I_a \phi_t \tau)^2 \quad (10)$$

where ϕ_t is the fluorescence efficiency, k_a the annihilation rate constant, I_a the rate of light absorption, ϕ_t the triplet formation efficiency, and τ is the triplet lifetime. The three quantities ϕ_t , ϕ_t , I_a , it was argued,⁷³ are unlikely to be field-dependent because they are properties of diamagnetic materials (although the peculiar properties of carbon disulphide referred to above indicate that that may be a false argument in special circumstances). In support of this view Faulkner and Bard draw attention to solid-state results which show that magnetic fields do not affect the intensity of the prompt fluorescence from crystalline anthracene. The concentration dependence of the fluorescence and its magnetic field dependence allows this argument to be taken further. In solutions containing an anthracene concentration of $> ca. 10^{-4} \text{ mol dm}^{-3}$, anthracene triplet lifetimes are shortened drastically by self- or impurity-quenching. At lower concentrations the lifetime is virtually constant. Any field dependence of the lifetimes would probably be concentration dependent in the range where the quenching term begins to be significant in determining the value of τ . Thus the field effect that arose from this source would be expected to be concentration dependent in this range. Since the experimental results show that the field variation is independent of concentration in the range where the lifetime begins to change markedly, it is most unlikely that the lifetime τ is the field-dependent quantity.

Faulkner and Bard also go on to eliminate ϕ_t as the field-dependent quantity.⁷³ They examined the fluorescence of a solution of $5 \times 10^{-5} \text{ mol dm}^{-3}$ anthracene plus $7 \times 10^{-4} \text{ mol dm}^{-3}$ phenanthrene in DMF and found that the field dependence of the anthracene-delayed fluorescence was the same as in the absence of the phenanthrene sensitizer. In this case the anthracene triplet is populated by energy transfer rather than intersystem crossing from anthracene singlet, and therefore ϕ_t cannot be the field-dependent factor. The elimination of τ , ϕ_t , I_a , and ϕ_t as the field-sensitive quantities leaves only k_a , and the theoretical reasons for its dependence have already been explained.

The role of doublet species in modifying the field dependence of the delayed fluorescence has also been elucidated⁷⁴ and, as indicated previously, centres on the suggestion made by Hoytink⁷⁵ that ion radicals might be effective triplet quenchers in fluid solution. Faulkner and Bard⁷⁴ measured the intensities and lifetimes of the delayed fluorescence from anthracene and WB perchlorate in methylene chloride solution. The effectiveness of WB^+ as a quencher of anthracene triplets was indicated by the shortening of their lifetimes. For example, a $1.8 \times 10^{-7} \text{ mol dm}^{-3}$ WB perchlorate and $8 \times 10^{-5} \text{ mol dm}^{-3}$ anthracene solution showed a delayed fluorescence lifetime of 1.4 ms, in contrast to a lifetime of 6.4 ms in the absence of WB^+ . The quenching rate constant was $ca. 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is comparable to the triplet-triplet energy-transfer rate constant in solvents of similar viscosity. As for the

⁷³ L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, 1969, **91**, 6495.

⁷⁴ L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, 1969, **91**, 6497.

⁷⁵ G. J. Hoytink, *Discuss. Faraday Soc.*, 1968, **45**, 14.

magnetic field effect it was found that the fluorescence intensity was enhanced (by ca. 2% in 0.8 T), as would be expected on the basis of the theory already explained. The longer lifetimes that result from this effect dominate the opposing effect on the annihilation rate. The results also suggest that the quenching rate is not entirely diffusion controlled,⁷⁴ and the authors suggest a tentative upper limit of $2.6 \times 10^{10} \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ on the rate constant.

Magnetic field effects on the fluorescence intensity from anthracene, DPA, rubrene, 1,3,4,8-tetraphenylpyrene (TPP), and fluoranthrene have also been reported.⁷⁶ Enhancements of the emission to the extent of up to 27% were noted for energy-deficient oxidations of anthracene, DPA, rubrene, and TPP anions by WB^+ , for the energy-deficient oxidation of fluoranthrene anion by the radical cation of 10-methylphenothiazine, and for the energy-deficient reduction of the rubrene radical cation by the *p*-benzoquinone radical anion.⁷⁷ In contrast (but in conformity with theory), no field effect was observed for the fluorescence arising from the energy-sufficient $\text{DPA}^+/\text{DPA}^-$ reaction. The field enhanced the luminescence from the reaction between the rubrene anion and cation radicals, but had no effect on the TPP anion and cation reaction. All these results are compatible with the inhibition of the triplet-triplet step by a magnetic field, the inhibition of the triplet-doublet radiationless quenching step, and the absence of involvement of triplet species in energy-sufficient systems. The rubrene⁺/rubrene⁻ and the TPP⁺/TPP⁻ systems are marginal cases, and it was suggested⁷⁶ that the former gives rise to luminescence predominantly *via* the triplet mechanism, but the latter is essentially energy-sufficient and forms the emitting state directly. The paper includes a useful list of reaction enthalpies and spectroscopic data and rationalizes the magnetic field effects by reference to the Johnson-Merrifield solid-state mechanism.

Oxygen is an obvious candidate for the examination of magnetic field effects on triplet species and its role in the production of delayed fluorescence from anthracene and pyrene in fluid solution has been studied.⁷⁸ The triplet quenching can be represented by the simple scheme



and its rate should be field dependent. The authors observed that the usual decrease of fluorescence intensity with applied field was modified when oxygen was admitted to the solution. At first no delayed fluorescence signal was detected but after several minutes its intensity increased to a measurable level. The same kind of time-dependent increase has also been noticed in solid samples and is probably caused by oxygen depletion arising from the formation of a transannular peroxide. The delayed fluorescence signals from both anthracene and pyrene increased with increasing field, indicating a magnetic inhibition of the quenching reaction just as in the case of radical ion quenching. On the other hand, in acetonitrile solution no change in the fluorescence was observed for either species although oxygen quenching was shown to be occurring by the decrease in lifetime of the aromatic triplet.

Further papers in this series deal with a series of related observations. One⁷⁹

⁷⁶ L. R. Faulkner, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, 1972, **94**, 691.

⁷⁷ H. Tachikawa and A. J. Bard, *Chem. Phys. Letters*, 1974, **26**, 10.

⁷⁸ H. Tachikawa and A. J. Bard, *J. Amer. Chem. Soc.*, 1973, **95**, 1672.

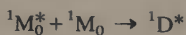
⁷⁹ C. P. Kesthelyi, N. E. Tokel-Takvoryan, H. Tachikawa, and A. J. Bard, *Chem. Phys. Letters*, 1973, **23**, 219.

examines the effect of the supporting electrolyte concentration and the magnetic field effect on a 9,10-dimethylantracene (DMA)–tri-*p*-tolylamine (TPTA) system dissolved in tetrahydrofuran (THF). The magnetic field enhanced the fluorescence for all concentrations of the supporting electrolyte tetra-*n*-butylammonium perchlorate (TBAP), and extrapolation to zero TBAP concentration gave results in accord with those of Weller and Zachariasse.⁸⁰ Although quenching of intermediates by TBAP ions might be important, the authors believe that the effect on the reaction enthalpy as the concentration of TBAP decreases is probably more important. This increase in ΔH can be traced either to a decrease in the extent of formation of the ion pairs $(\text{TBAP})^+\cdots(\text{DMA})^-$ or $(\text{TPTA})^+\cdots\text{ClO}_4^-$ (formation of ion pairs would facilitate the oxidation of TPTA and the reduction of DMA, and hence reduce ΔG^\ominus for the ion annihilation reaction), or to a change in the nature of the solvent system with an effective increase in relative permittivity at higher TBAP concentrations. Thus at low TBAP the reaction is strongly energy deficient and proceeds through the magnetically sensitive triplet annihilation route, but at high TBAP concentrations the reaction may proceed through the direct production of singlets and be less magnetically sensitive.

The effect of solvents has been studied^{71,81} by measuring the emission intensity of rubrene ions generated electrochemically. The intensity increases with applied field and the effect is strongest when the solvent is DMF and then progressively weaker along the sequence acetonitrile, benzonitrile, THF. The results were interpreted⁸¹ in terms of a model in which the electron-transfer route produces both singlet and triplet excited states of rubrene with the triplets being quenched by radical ions or oxygen. The authors examined the energetics of the reaction on the basis of Marcus's theory of electron transfer, and suggest the possibility that two triplet states may be formed in the electron-transfer step.

Wyrsh and Labhart,⁸² Tachikawa and Bard,⁸³ and van Willigen⁴⁶ have all examined the delayed fluorescence from monomer and excimer species. Wyrsh and Labhart investigated 1,2-benzanthracene in ethanol, van Willigen investigated pyrene in 3-methylpentane and in ethanol, and Tachikawa and Bard pyrene and 1,2-benzanthracene, the pyrene–TMPD system, and the 9-methylantracene–TPTA system.

Wyrsh and Labhart observed different magnetic quenching behaviour of the monomer and excimer emissions and concluded that there is no common triplet annihilation process generating the two types of fluorescent species. On the other hand, van Willigen observed the same behaviour when 3-methylpentane was the solvent. van Willigen ascribes his results to a scheme proposed by Stevens⁸⁴ which involves the reaction sequence



⁸⁰ A. Weller and K. Zachariasse, *Chem. Phys. Letters*, 1971, **10**, 424, 590.

⁸¹ H. Tachikawa and A. J. Bard, *Chem. Phys. Letters*, 1974, **26**, 246.

⁸² D. Wyrsh and H. Labhart, *Chem. Phys. Letters*, 1971, **8**, 217.

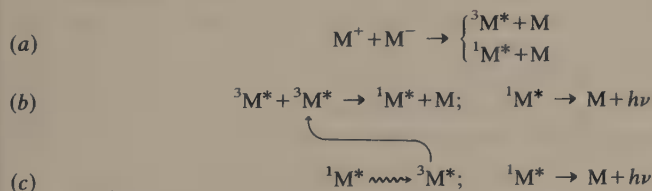
⁸³ H. Tachikawa and A. J. Bard, *Chem. Phys. Letters*, 1974, **26**, 568.

⁸⁴ B. Stevens, *Chem. Phys. Letters*, 1969, **3**, 233.

The first step is common to excimer ($^1D^*$) and excited monomer ($^1M_0^*$) formation; it is a spin-selective step and therefore the magnetic field ought to affect the two fluorescent intensities equally. He attempts to account for the discrepancy between the two sets of results on two grounds. First, that the mechanism depends on the species involved. Second, and much more speculatively, that the exciplex formation step (the second of the three steps in the scheme above) depends on the relative orientations of the species, orientations that are influenced by the magnetic field. It is hard to believe that this could be the explanation, even at low temperatures where rotational correlation times are quite long, but it is at least an interesting suggestion. Tachikawa and Bard observe that the magnetic field effects on the excimer and monomer delayed fluorescence intensities are essentially the same for pyrene in cyclohexane and for 1,2-benzanthracene in cyclohexane, and also conclude that there must be a common precursor in these systems.

van Willigen⁴⁶ has also reported a peculiar field dependence when ethanol is used as solvent. At low temperatures the monomer and dimer fluorescences *increase* with magnetic field. He suggests that the reason might lie in the formation of doublet radicals in the system, and that these act as triplet quenchers (the remark on p. 75 arose from this suggestion).

Magnetic field effects have also been observed in tetracene-TMPD,⁸⁵ this energy-deficient system showing an intensity increase of up to 19.5% in fields of up to 0.75 T, and the results were interpreted as evidence for the production of triplet tetracene by charge transfer between tetracene radical anion and TMPD cation. The delayed fluorescence of carbazole in DMF with t-butylammonium iodide as supporting electrolyte shows a sharp increase in intensity up to *ca.* 0.4 T, and this is followed by a gradual decline.⁸⁶ Perisamy and Santhanam⁸⁷ have also examined the electrochemiluminescence of mixed systems in which phenanthrene and perdeuteriated phenanthrene provide the radical anion, and propose a triplet-triplet annihilation step on the basis of the magnetic field effect observed. A magnetic field effect on an energy-sufficient system has also been reported.⁸⁸ The authors studied the rubrene, tetracene, phenanthrene, and cation-anion systems and found an increase in fluorescent intensity of the order of 10% in 1 T. The overall scheme can be summarized by the sequence



Step (b) is the conventional, magnetic-field-sensitive step, but triplet species generated by the singlet step (c) may also take part in it and give rise to an overall magnetic field dependence, especially if step (c) is itself magnetic field dependent. Thus if a magnetic field can inhibit the crossing involved in step (c) more of the initial singlets can produce fluorescence.

⁸⁵ H. Tachikawa and A. J. Bard, *Chem. Phys. Letters*, 1973, **19**, 287.

⁸⁶ K. S. V. Santhanam, *Canad. J. Chem.*, 1971, **49**, 3577.

⁸⁷ N. Perisamy and K. S. V. Santhanam, *Canad. J. Chem.*, 1975, **53**, 76.

⁸⁸ N. Perisamy, S. J. Shah, and K. S. V. Santhanam, *J. Chem. Phys.*, 1973, **58**, 821.

Finally we report an interesting application of this type of magnetic field effect on a solid polymer (which is as close to true solids as we allow ourselves to come in this review). Avakian *et al.*⁸⁹ have found that the rate of fusion of triplet exciton pairs in polymers such as poly(vinylnaphthalene) can be changed by a magnetic field of a few kilogauss. The delayed fluorescence following exciton generation was found to increase monotonically to 3% above the zero-field value at 0.09 T (900 G), and then to drop back to its zero-field value at 0.4 T. The emission continues to decrease to an asymptotic value *ca.* 2% below the zero-field value when the field reaches 1.0 T. This behaviour contrasts with the observation of a similar phenomenon in naphthalene at 77 K, where the low-field peak (of 6%) occurs at 0.06 T, the zero-field value is passed at 0.17 T, and the saturation value (of -12%) is attained above 1.0 T. The authors explain these observations in terms of the local orientations of the naphthalene units along the polymer chain, and reach the significant conclusion that they are spread over a range of orientations such that $S_x^2 - S_y^2$ averages to zero but that the normal axes of each naphthalene unit remain approximately aligned. This magnetic field dependence therefore constitutes a novel method for investigating the conformation of polymer molecules. Essentially the technique consists of deducing the fine-structure parameters D and E from the magnetic field dependence of delayed fluorescence. Deviations from the known parameters of the isolated molecules can then be accounted for by assuming a conformation and then allowing for the averaging of differently ordered side-groups by the exciton motion.

5 Conclusion

It should be clear at this point that there are many well-authenticated examples of the effect of magnetic fields on chemical reactions; effects that range from the inhibition of spin-multiplicity crossings and the consequent effects on fluorescent activity (and, presumably, on reactions themselves) to the actual modification of the concentrations of the product species. A magnetic field is potentially an influence on any reaction involving the change of multiplicity of some intermediate, and whether that change of multiplicity leads on to a physical consequence (fluorescence) or to a chemical consequence (cage, escape reactions) is not of itself of interest. The rate constants of all the steps in the overall scheme must be appropriate, but in many cases that is happily the case. So many reactions involving doublet and triplet (and presumably higher multiplets) are magnetically sensitive that the best advice a theoretician can give to the experimentalist with a likely candidate is: try it! Although we have emphasized the academic and theoretical aspects of magnetic field effects it should be clear that they may have considerable industrial significance. We shall have to wait in order to see whether this will emerge through their application to polymerization reactions, or to the separation of nuclear isotopes, or simply to the warping of a reaction in favour of one stereoisomer or product of a radical reaction.

Note added in proof. Although an earlier analysis of the singlet and triplet photosensitized decomposition of dibenzoyl peroxide showed no field effect,⁹⁰ a new study using much higher fields⁹¹ has shown that there is one.

⁸⁹ P. Avakian, R. P. Groff, A. Suna, and H. N. Cripps, *Chem. Phys. Letters*, 1975, **32**, 466.

⁹⁰ H. Sakuragi, M. Sakuragi, T. Mishima, S. Watanabe, M. Hasegawa, and K. Tokumaru, *Chem. Letters*, 1975, **8**, 231.

⁹¹ Y. Tanimoto, H. Hayashi, S. Nagakura, H. Sakuragi, and K. Tokumaru, in press.

PART II
INORGANIC CHEMISTRY

5 Introduction

By M. F. LAPPERT

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The general form of the 1975 *Annual Reports* (Vol. 72) on Inorganic Chemistry shows significant changes from previous years. Even greater note than hitherto is taken of the existence of the *Specialist Periodical Reports* series. Individual volumes of these now provide comprehensive coverage of *inter alia* Main-group Element Chemistry, Inorganic Chemistry of the Transition Elements, Organometallic Chemistry, Electronic Structure and Magnetism of Inorganic Compounds, Inorganic Reaction Mechanisms, Spectroscopic Properties of Inorganic and Organometallic Compounds, and Radiochemistry. Furthermore, the Publications Committee of the Chemical Society has recommended a substantial decrease in the size of the *Annual Reports*.

A deliberate attempt has therefore been made to offer a quite distinct form of coverage of progress in inorganic chemistry from that of the *Specialist Periodical* monographs, which give a comprehensive – but inevitably terse – summary of advances in the subject, and provide a particularly convenient secondary source of literature for the researcher. Our aim is to appeal more to generalists, including the members of staff of University or Polytechnic Chemistry Departments in their capacities as teachers, rather than as research workers, who wish to keep themselves and their students abreast of important developments in all branches of the subject.

We have tried to cover rather fewer areas than in former years, but in greater detail than has been possible hitherto. Selected topics, rather than papers, have been chosen and in the main these represent areas in which there has been a considerable activity during the year. Where feasible, for each topic chosen for comment, one or two key references to work prior to 1975 have been made. Each author was asked to restrict the number of references cited relative to the amount of descriptive material. For this reason there is very limited mention of books or review articles. The choice of material is necessarily subjective and to some extent reflects the interest of the contributors. We are conscious of the fact that much fine work has not been covered and we wish to have this contribution considered as the first of a short series. In subsequent years, a deliberate attempt will be made to cover fields which have been neglected in the present volume. Aspects of the non-organometallic chemistry of the lanthanides and actinides are omitted this year, but will be dealt with in the 1976 *Reports*.

In the organometallic section, we have kept in mind that *Annual Reports Section B* also deal with this topic, although there the appeal is intended to be primarily to the organic chemist. We do not particularly accept the desirability for boundaries between the various areas of chemistry, but simply recognise that, with limited space,

duplication of coverage is undesirable. Drs. Cardin and Dixon have therefore concentrated on aspects of structure and synthesis and less on the use of organometallic compounds as reaction intermediates or as catalysts. For example, the topic of hydroboration is omitted from this volume. Discussion of metal carbonyls and aspects of transition-metal hydride chemistry is found in this section.

Among the books published in 1975 or to the close of 1974 are the SI edition of an important undergraduate text,¹ and a monograph² on inorganic solids, also principally of interest to teachers and students. The Pergamon multivolume reference work³ 'Comprehensive Inorganic Chemistry', written by a formidable international group of inorganic chemists, has now been made available in 27 separate titles in hard- and soft-backed editions, often *ca.* 150 pages long dealing with single elements, groups of elements, or groups of compounds, *e.g.*, tungsten bronzes. In addition to the *Specialist Periodical Reports*, 1975 saw the publication of a parallel series published commercially.⁴ We also note the appearance of a number of specialist monographs.⁵⁻¹³

¹ J. E. Huheey, 'Inorganic Chemistry; Principles of Structure and Reactivity', Harper and Row, New York, 1975, 1972 edition with SI unit alterations.

² D. M. Adams, 'Inorganic Solids', John Wiley, New York, 1974.

³ 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. S. Nyholm and A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1974 (Vols. 1-5).

⁴ M. T. P. International Review of Science: Inorganic Chemistry, Series 2, eds. M. F. Lappert, D. W. Sowerby, V. Gutmann, B. J. Aylett, D. W. A. Sharp, M. Mays, K. W. Bagnall, A. G. Maddock, M. L. Tobe, and L. E. J. Roberts, of Vol. 1-10, respectively, Butterworths, London, 1975.

⁵ D. E. Corbridge, 'Structural Chemistry of Phosphorus', Elsevier, Amsterdam, 1974.

⁶ S. A. Cotton and F. A. Hart, 'The Heavy Transition Elements', Macmillan, London, 1975.

⁷ Gmelin, 'Handbuch der Anorganische Chemie', Vol. 24, Part 3, 'Perfluorohalogenverbindungen von P, As, Sb, and Bi', Springer, Berlin, 1975.

⁸ 'Dynamic Nuclear Magnetic Resonance Spectroscopy', ed. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975.

⁹ 'Techniques and Topics in Bioinorganic Chemistry', ed. C. A. McAuliffe, Macmillan, London, 1975.

¹⁰ F. J. McQuillin, 'Homogeneous Catalysis in Organic and Inorganic Chemistry', ed. R. Ugo, D. Reidel, Dordrecht-Holland, 1975.

¹¹ 'Boron Hydride Chemistry', ed. E. L. Muetterties, Academic Press, New York, 1975.

¹² T. Onak, 'Organoborane Chemistry', Academic Press, New York, 1975.

¹³ M. J. Taylor, 'Metal-to-Metal Bonded States of the Main Group Elements', Academic Press, New York, 1975.

6 The Typical Elements

By A. J. CARTY

*Guelph-Waterloo Centre for Graduate Work in Chemistry,
Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1*

R. H. CRAGG

Department of Chemistry, University of Kent, Canterbury, CT2 7NH

J. D. SMITH

School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ

PART I: Groups I and II

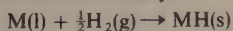
By R. H. Cragg

1 Group I

One of the major areas of interest in Group I chemistry has been the detailed study of the reactions of alkali metals with hydrogen. The significance of this work arises from the knowledge that in the reactions of alkali metals with hydrocarbons the metal hydride is a possible significant intermediate and it is therefore of importance to have some understanding of these alkali-metal hydrides.

For example, in the self-hydrogenation of alkynes and alkenes at the surface of liquid sodium, molecular hydrogen is formed and the rate at which it is subsequently converted into metal hydride is influenced by the nature of the hydrocarbon.

Liquid alkali metals react with hydrogen to form hydrides at the surface and, because the reaction is moderately slow at temperatures just above the melting point of the metal, it is relatively easy to measure the rate of the reaction by following the decrease in hydrogen pressure manometrically:



The results for the reaction between hydrogen and liquid sodium have been previously reported and, in order to obtain comparisons with other alkali metals, the rate of adsorption of hydrogen at liquid lithium and potassium surfaces has been determined in the absence of hydrocarbons. The experimental technique used for the study of the reaction of hydrogen with alkali metals is relatively straightforward. A jet of the clean metal is continuously injected into hydrogen and the rate of reaction of hydrogen with the metal surface is measured over a selected temperature and pressure range, *e.g.*, in the case of potassium, 22.2–0.3 kN m⁻² and 210–333 °C.¹ The reaction between hydrogen and potassium is observed to follow first-order kinetics with an activation energy of 66.5 kJ mol⁻¹, a slightly higher value than that reported for sodium (see Table). In contrast, potassium is observed to react

¹ G. Parry and R. J. Pulham, *J.C.S. Dalton*, 1975, 446.

with hydrogen approximately four times faster than with sodium, which is a little surprising in view of the chemical similarities of the two metals. It was therefore suggested that, in view of the similar activation energies of sodium and potassium, the rate-determining step in their reaction with hydrogen is the same and probably involves electron transfer from the metal to adsorbed hydrogen atoms. This proposal is consistent with the observation that the free energies of formation of the two hydrides are similar and that the dissociative adsorption of hydrogen is usually rapid. The mechanism of the reaction is suggested to proceed by successive steps, viz. the conversion of gaseous molecular hydrogen into crystalline potassium hydride with dissociation into atoms and the formation of hydride anions. The adsorbed hydride ions can either dissolve in the metal or, alternatively, if the potassium is saturated, potassium hydride crystals nucleate and grow on the surface of the potassium:



It therefore seems reasonable to suggest that the difference in the rates of reaction of hydrogen with potassium and with sodium is mainly due to the relative strength of hydrogen adsorption; the more strongly the atom is adsorbed, the easier becomes the electron transfer, and the results indicate that hydrogen is more strongly adsorbed on potassium than on sodium.

The rates of reaction of hydrogen with a clean liquid lithium surface have also been studied; the reaction is first order with an activation energy of 52.8 kJ mol^{-1} .² Lithium was found to react, at 250°C , about forty times faster than sodium with hydrogen, and this result supports previous observations which showed that the addition of small amounts of lithium to sodium increases the rate of hydrogen adsorption. As in the case of potassium, the rate-determining step in the reaction of hydrogen with lithium is assigned to the electron transfer from the metal to adsorbed hydrogen atoms. In view of the faster reaction in the case of lithium it appears that hydrogen is more strongly adsorbed on lithium than on either sodium or potassium.

The reaction of hydrogen with solutions containing lithium, strontium, or barium is faster than with sodium.³ The rate is directly proportional to the hydrogen pressure and the reaction is first order with respect to the hydrogen pressure provided that the solution composition and the liquid-metal surface remain constant throughout the reaction. The results suggest that the hydrogen molecule is directly involved in the rate-determining step. However, it is important to note that the observed changes in the rate constants are not accounted for only by the activation energy changes as the pre-exponential factor changes with both the solute metal and its concentration. Reported values for the activation energies and rate constants for the reaction of liquid metals with hydrogen are given in the Table.

Table

| Metal | $E^*/\text{kJ mol}^{-1}$ | $k(250^\circ\text{C})/\text{mm s}^{-1} (\text{kN m}^2)^{-1}$ |
|--------------|--------------------------|--|
| Na | 72.4 | 2.505×10^{-7} |
| Na-Li (5.0%) | 64.1 | 5.860×10^{-7} |
| K | 66.5 | 9.010×10^{-7} |
| Li | 52.8 | 1.065×10^{-5} |
| Na-Ba (5.0%) | 45.0 | 4.821×10^{-5} |

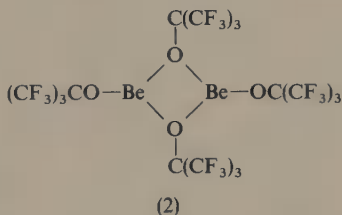
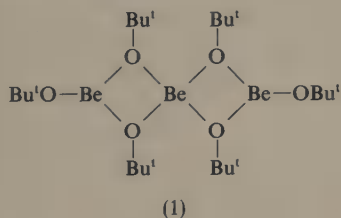
² G. Parry and R. J. Pulham, *J.C.S. Dalton*, 1975, 1915.

³ M. R. Hobdell and A. C. Whittingham, *J.C.S. Dalton*, 1975, 1591.

Recently, the reaction of liquid potassium with ethylene has been investigated over the range 503—671 K by measuring the pressure changes and analysing the gas as the metal is injected into hydrogen, using an electrical pump.⁴ It is observed that at lower temperatures self-hydrogenation takes place. The amount of ethane produced decreases as the temperature increases and it is suggested that this is due to the loss of hydrogen from the surface by dissolution in the metal.

2 Group II

Alkoxy-derivatives of beryllium are usually associated, in keeping with the general property of beryllium to be four-co-ordinate where possible. For example, dimethoxyberyllium is polymeric and insoluble in hydrocarbon solvents. Even di-*t*-butoxyberyllium, which is soluble in hydrocarbon solvents, is trimeric (1) and the only monomeric alkoxide so far reported is bis(2,6-di-*t*-butylphenoxy)beryllium. Recently, a dimeric alkoxide of beryllium, bis(nonafluoro-*t*-butoxy)beryllium (2), one of the most volatile alkoxides known (it sublimes *in vacuo* at room temperature), has been obtained from the interaction of nonafluoro-*t*-butyl alcohol and diethylberyllium.⁵ Although insoluble in benzene, (2) dissolves without reaction in nitrobenzene and is dimeric in hexafluorobenzene. The lack of extensive association can be attributed to the increase in steric hindrance about the beryllium atom. Rather surprisingly, the bridge Be—O bond in the dimer is cleaved by diethyl ether. This is in contrast to the lack of reaction with pyridine or quinuclidine of (1), the hydrogen analogue of (2).



The reaction of sodium nonafluoro-*t*-butoxide with beryllium(II) chloride in diethyl ether results in the formation of a distillable liquid, $\text{Be}[(\text{CF}_3)_3\text{CO}]_2, \text{OEt}_2$, which is monomeric in benzene and only the second example of a three-co-ordinate monomeric beryllium alkoxide. On reaction with pyridine or ammonia the first examples of 1:2 beryllium complexes are obtained.

PART II: Group III

By A. J. CARTY

1 Boron

Boron Hydrides and Borane Anions.—*Theoretical Studies of Bonding and Structure.* It is refreshing to find a paper in which theoretical calculations are used to predict

⁴ G. Parry and R. J. Pulham, *J.C.S. Dalton*, 1975, 2576.

⁵ R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1975, 1244.

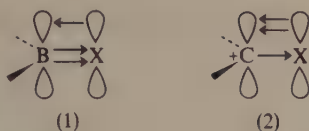
chemical behaviour rather than to rationalize, *post facto*, experimental observations. In an important contribution from Lipscomb's laboratory ground-state charge distributions derived from minimum basis set Slater orbital calculations using the PRDDO approximation have been employed to predict likely sites of electrophilic and nucleophilic attack in B_8H_{12} , $B_{10}H_{14}$, $[B_{11}H_{13}]^{2-}$, related boranes, and carboranes.^{1a} Reactivity predictions are based on relative values of inner-shell eigenvalues, Mulliken atomic and group charges, and, in addition, sums of populations over the several highest occupied MO's. Such calculations can be an invaluable aid in rationalizing reaction sequences or devising routes to boron hydride derivatives, although it must be remembered that orbital symmetry correlations are ignored. In the past similar calculations have proved of significant value in decaborane(14) chemistry. For B_8H_{12} , electrophilic attack is predicted to occur preferentially at B-2 while B-7 is most susceptible to nucleophilic substitution. For $[B_8H_{13}]^-$, electrophilic substitution should occur in the order $B-4 > B-2 \approx B-1 > B-3 > B-7$ and a facile loss of H^- from either B-4 or B-5 should yield B_8H_{12} . In several cases [e.g. in B_8H_{14} (C_s symmetry), where charge criteria indicate B-3 as a site for nucleophilic attack but eigenvalue differences do not differentiate between B-3 and B-7 sites] an unequivocal distinction between two possible sites of attack cannot be made. Here experimental results will be particularly significant in refining the model.

The same paper analyses structural interrelationships between several B_8 – B_{11} hydride species on the basis of detailed examination of localized molecular orbitals (LMO's). Topological and LMO descriptions generally correlate quite well.

In the context of *ab initio* LMO theory for boron hydrides, it is significant that experimental confirmation of the validity of this approach has been obtained from measurements of the Compton profile of decaborane(14).^{1b} There is excellent agreement between the experimental and calculated electron momentum distributions in this molecule, showing that the wavefunctions used in constructing LMO's are 'good'. *Ab initio* MO calculations on seventeen small boron compounds have been carried out for comparison of geometries, bonding preferences, and stabilities with isoelectronic carbocations.^{1c} These calculations lend quantitative support to many intuitive predictions. Thus, for example substitution of H in BH_3 by a π -donor group X (NH_2 , OH, or F) stabilizes BH_2X relative to BH_3 by 53–58 kcal mol⁻¹, while hyperconjugation in H_2BCH_3 gives only 12 kcal mol⁻¹ of stabilization energy and adduct formation H_3N, BH_3 21 kcal mol⁻¹. Similarly H_2NBH_2 and H_2BOH are predictably planar with B–N and B–O multiple bonds and with non-rigid rotational barriers about B–N and B–O bonds of 29 and 144 kcal mol⁻¹ respectively.

Geometries of boron compounds and isoelectronic carbocations (e.g. $HB=CH_2$ and the classical vinyl cation $CH_2=\dot{C}H$) are generally similar, but in terms of bonding boron is a stronger σ -donor and weaker π -acceptor than positively charged carbon. This comparison is best represented by the major resonance structures (1) and (2). Where experimental data are available for comparison the 6-31G* calculations appear to give a better overall level of agreement than previous calculations.

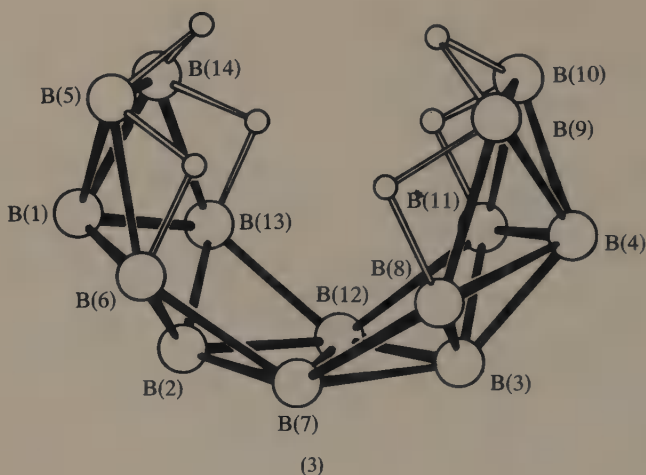
¹ (a) J. H. Hall, jun., D. A. Dixon, D. A. Kleier, T. A. Halgren, L. D. Brown, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1975, **97**, 4202; (b) I. R. Epstein, P. Pattison, M. G. H. Wallbridge, and M. J. Cooper, *J.C.S. Chem. Comm.*, 1975, 567; (c) J. D. Hill, P. von R. Schleyer, and J. A. Pople, *J. Amer. Chem. Soc.*, 1975, **97**, 3402; (d) E. L. Muetterties, E. L. Hoel, C. G. Salentine, and M. F. Hawthorne, *Inorg. Chem.*, 1975, **14**, 950; (e) E. L. Muetterties and B. F. Beier, *Bull. Soc. Chim. belges*, 1975, **84**, 397.



The borane anions $[B_nH_n]^{2-}$ present a unique opportunity for the study of rearrangement mechanisms and dynamics among the various classes of stereochemically non-rigid molecules. These ions incorporate two nuclei (^1H and ^{11}B) which are excellent n.m.r. probes and in atomic and electronic terms are relatively simple molecules lending themselves to sophisticated MO calculations. Several experimental observations^{1d} concerning rearrangement barriers in these ions have been clarified *via* extended Huckel MO calculations.^{1e} Key features of polytopal isomerism for the family $[B_nH_n]^{2-}$ are: (i) $[B_8H_8]^{2-}$, dodecahedral in the solid state, fluxional in solution with rearrangement occurring between square-antiprismatic and bicapped trigonal-prismatic isomers; (ii) $[B_{11}H_{11}]^{2-}$, subject to rapid intramolecular rearrangement in solution even at low temperatures; (iii) $[B_7H_7]^{2-}$, a rigid, pentagonal-bipyramidal structure in solution over a wide temperature range; (iv) $[B_9H_9]^{2-}$, a much larger rearrangement barrier than for $[B_8H_8]^{2-}$, being essentially rigid up to 200 °C. These apparently conflicting facts can be rationalized by consideration of MO energies in the various polyhedral forms of the ions. For $[B_8H_8]^{2-}$ calculations indicate a small energy gap between the highest occupied and lowest unoccupied MO's in all of the possible D_{2d} , D_{4d} , and C_{2v} forms. Facile rearrangement of all three forms can occur *via* normal vibrational modes. By contrast the gap is large for $D_{5h}[B_7H_7]^{2-}$ and this anion cannot rearrange *via* the degenerate C_{2v} isomer. The most likely intermediate (C_{4v} , $[B_9H_9]^{2-}$) in the rearrangement of D_{3h} ground-state $[B_9H_9]^{2-}$ is degenerate. This may explain the apparently anomalously high barrier to interconversion in this species. However, for $[B_{11}H_{11}]^{2-}$ the presence of a degeneracy in the C_{5v} form suggests that the lower-symmetry C_s isomer may be a more reasonable transition state. It will be interesting to see whether predictions of fluxionality in co-ordination compounds ML_7 , ML_8 , and ML_9 based on generalization of the borane anion rearrangement processes, are borne out in subsequent work; there is evidence that ML_8 complexes have very low rearrangement barriers. Incorporation of heteroatoms (carbon or metal atoms) into a *closoborane* framework might be expected to complicate rearrangement processes. This appears to be the case for metallocarbaboranes (see below).

Structure of Boranes. The new boron hydride tetradecaborane(20), synthesized *via* reaction of excess octaborane(12) with potassium nonahydrohexaborate in ether followed by treatment with HCl at -78 °C, is a yellow crystalline solid for which X-ray data, collected at -164 °C, indicate structure (3).^{2a} The molecule consists of two B_8H_{12} fragments fused at the B-7—B-12 positions with their open faces *cis* to one another. This molecule thus joins a growing number of boranes with structures built up by fusing two different borane fragments across a common edge. Examples include $B_{13}H_{19}$, $B_{16}H_{20}$, *n*- $B_{18}H_{22}$, and *i*- $B_{18}H_{22}$. The hydride $B_{14}H_{18}$ recently

² (a) J. C. Huffman, D. C. Moody, and R. Schaeffer, *J. Amer. Chem. Soc.*, 1975, **97**, 1621; (b) S. Hermanek, K. Felter, J. Plešek, L. J. Todd, and A. R. Garber, *Inorg. Chem.*, 1975, **14**, 2250; (c) J. D. Weiser, D. C. Moody, J. C. Huffman, R. L. Hilderbrandt, and R. Schaeffer, *J. Amer. Chem. Soc.*, 1975, **97**, 1074.

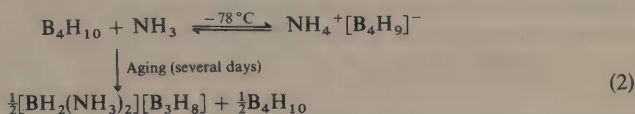


characterized by ^{11}B and ^2H n.m.r. may be of this type,^{2b} with decaborane and hexaborane frameworks fused across one edge. The existence of other hydrides with decaborane fragments linked to lower polyhedra seems possible.

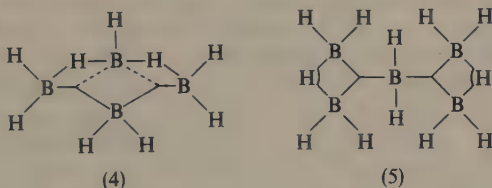
Interesting structural results relevant to the problem of boron-substituent bonding in substituted boranes have been obtained. Thus, the postulate that π -bonding interactions between fluorine ($2p_\pi$), silicon ($3p_\pi$ and $3d_\pi$), and the boron cage may be responsible for the known stability sequences $2\text{-FB}_5\text{H}_8 > 1\text{-FB}_5\text{H}_8$ and $1\text{-SiH}_3\text{B}_5\text{H}_8 > 2\text{-SiH}_3\text{B}_5\text{H}_8$ has been supported by extended Hückel MO calculations. (The 1-SiH₃-isomer is favoured over the 2-isomer by *ca.* 0.4 eV.) In direct contrast, whereas isomerization studies show a stability order $2\text{-MeB}_5\text{H}_8 > 1\text{-MeB}_5\text{H}_8$, calculations yield a negligible π -bond order for the B—C bond; hence B—C π -bonding is an unlikely source of stabilization. It is comforting to know that these results are borne out by *subsequent* electron diffraction results.^{2c} The Si—B bond length in 1-SiH₃B₅H₈ [1.981(5) Å] is indeed significantly shorter than the corresponding length in the 2-isomer [2.006(4) Å] while the B—C bond lengths in 1-MeB₅H₈ [1.595(5) Å] and 2-MeB₅H₈ [1.592(5) Å] are essentially identical.

Synthesis and Structures of Borane Anions. The Brönsted acidity of boron hydrides is now well established. Abstraction of a bridging proton followed by insertion of an electrophile into the 'bare' boron-boron bond results in polyhedral expansion and is a useful synthetic method for borane anions or, indeed, metallocboranes. The *nido* carbaborane anion $[2,3\text{-C}_2\text{B}_4\text{H}_7]^-$ undergoes quite analogous reaction sequences. Recent *Annual Reports* have illustrated the scope of these insertions. An important paper pertaining to properties and structures of borane anions derived in this way has now appeared.³ Thus B₄H₁₀ can be deprotonated by potassium hydride or ammonia according to equations (1) and (2).

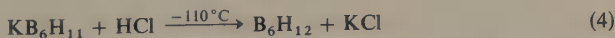
³ R. J. Remmel, H. D. Johnson, jun., I. S. Jaworinsky, and S. G. Shore, *J. Amer. Chem. Soc.*, 1975, **97**, 5395.



The competing hydrogen abstraction and cleavage implied in the latter reaction are notable and perhaps more general than previously suspected (*cf. Annual Reports* 1971–73). The anion $[\text{B}_4\text{H}_9]^-$ is dynamic at room temperature on the n.m.r. time-scale. The structure, represented in terms of Lipscomb's fractional three-centre B—B—B bonds, is shown in (4). More importantly the same paper describes



the anions $[\text{B}_5\text{H}_{12}]^-$, $[\text{B}_6\text{H}_{11}]^-$, and $[\text{B}_7\text{H}_{12}]^-$, produced *via* addition of BH_3 to the corresponding species $[\text{B}_4\text{H}_9]^-$, $[\text{B}_5\text{H}_8]^-$, and $[\text{B}_6\text{H}_9]^-$. The triphenylmethylphosphonium salts of $[\text{B}_5\text{H}_{12}]^-$ and $[\text{B}_6\text{H}_{11}]^-$ are white solids stable at room temperature for short periods. ^{11}B and ^1H n.m.r. spectra show that $[\text{B}_5\text{H}_{12}]^-$ is fluxional above -90°C but a static structure is apparent at -135°C . Topologically this ion has been represented as (5) and is a member of a new class of boron hydride species, the *hypho*-boranes containing $2n+8$ skeletal electrons. The *hypho* (Greek for net) structure can be compared with the increasingly open frameworks *closo* ($2n+2$) (e.g. $[\text{B}_{12}\text{H}_{12}]^{2-}$), *nido* ($2n+4$) (e.g. B_5H_9), and *arachno* ($2n+6$) (e.g. B_5H_{11}), as the number of skeletal electron pairs increases. The phosphine adducts $\text{B}_5\text{H}_9(\text{PMe}_3)_2$, described in last year's report (p. 181), and $\text{B}_6\text{H}_{10}(\text{PMe}_3)_2$ are also members of the *hypho*-boranes. The structure of the latter, not available at the time of writing, is apparently an open fragment of the equatorial belt of an icosahedron. Shore and co-workers³ also give details of their high-yield synthesis of B_5H_{11} and B_6H_{12} [equations (3) and (4)] briefly mentioned in the 1971 *Annual Report*. Finally, it has become clear from recent work that the relative acidities (Brönsted) of boron hydrides of a given class (e.g. *nido* or *arachno*) increase with increase in framework size.



Metalloboranes.—An excellent review of metalloborane chemistry published in 1974,^{4a} together with last year's Report, gives perspective to this rapidly expanding

⁴ (a) N. N. Greenwood and I. M. Ward, *Chem. Soc. Rev.*, 1974, **3**, 231; (b) B. P. Sullivan, R. N. Leyden, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1975, **97**, 455; (c) R. N. Leyden and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1975, 310; (d) K. Wade, *Chem. in Britain*, 1975, **11**, 177; (e) K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1975, **18**, in the press; (f) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, 1975, **14**, 751.

field of research. The major advance this year has been the synthesis of several *closo*-nickelaboranes derived from $[B_9H_{12}]^-$, $[B_{10}H_{10}]^{2-}$, and $[B_{11}H_{13}]^{2-}$.^{4b,4c} Synthetic methods generally involve reduction of an anion with Na-Hg in the presence of nickelocene or, for derivatives of $[B_{10}H_{10}]^{2-}$, direct reaction of the anion with $[\eta-C_5H_5Ni(CO)]_2$ or $[(\eta-C_5H_5)_3Ni_2]^{2+}$. Of the four compounds characterized, two, $Bu_4N[(\eta-C_5H_5)-1-Ni(B_{11}H_{11})]$ and $[(\eta-C_5H_5)_2-1,2-Ni_2(B_{10}H_{10})]$, have icosahedral structures^{4b} while $Me_4N[(\eta-C_5H_5)-2-Ni-(B_9H_9)]$ and $Me_4N[(\eta-C_5H_5)-1-Ni-(B_9H_9)]$ have bicapped square-antiprismatic structures with the nickel atoms in equatorial and apical positions, respectively.^{4c} By analogy with related metallocarboranes (see below), it might be expected that $Me_4N[(\eta-C_5H_5)-1-Ni-(B_9H_9)]$ would thermally rearrange to the 2-isomer where the metal has a higher-co-ordinate position. Rearrangement does occur, photochemically and thermally, but in the opposite sense, indicating that not only co-ordination number but also the charge densities on the boron atoms in the cage may be pertinent to the stability sequence. The existence of these polyhedra is predictable from electron-counting rules.^{4d,4e} For example, the hypothetical anion $[B_{10}H_{10}]^{6-}$ contains 13 skeletal electron pairs suitable for a 12-vertex polyhedron with two sites vacant. Incorporation of two formally $[\eta-C_5H_5Ni]^{3+}$ units (a neutral $\eta-C_5H_5Ni$ fragment contributes three electrons to a cluster) would be expected to produce a *closo*-icosahedron. Similarly the anion $[(B_{11}H_{11})Ni(C_5H_5)]^-$ is derived from the *nido*-species with one vacant site in an icosahedron. Clearly the existence of a vast number of metallocarboranes can be predicted using electron-counting rules and unquestionably there will be major developments in this area, paralleling the burgeoning chemistry of metallocarboranes.

Finally attention is drawn to a conceptually useful correlation^{4f} between the structures of *nido*-metallocarboranes and the boron hydride species which can be derived from the complexed hydroborate ion by addition or elimination of H^+ or BH_2^+ . For example $[B_3H_8]^-$, formally derived from B_4H_{10} by elimination of BH_2^+ , forms a complex $[Cu(PPh_3)_2B_3H_8]$ with a structure quite analogous to B_4H_{10} . Similarly, the B_6H_{10} molecule forms a complex $[Fe(CO)_4(B_6H_{10})]$ with a structure derived from that of $[B_6H_{11}]^+$ by removal of the proton bridging a basal B—B bond. Whether this model has general predictive utility remains to be seen.

Metal Complexes of the Tetrahydroborate Ion.—It has been known for many years that the 1H n.m.r. spectra of metal tetrahydroborate complexes provide little structural information since the bridge and terminal protons appear to be magnetically equivalent as a result of rapid intramolecular rearrangements. Structural assignments have thus been based mainly on vibrational spectroscopy and, where possible, X-ray analyses. Two groups have now independently observed separate resonances for bridge and terminal hydrogens in complexes containing bidentate $[BH_4]^-$ ions. Marks and Kolb^{5a} had previously observed that paramagnetism induced sufficient energy separation between exchanging proton sites in $[(C_5H_5)_3UBH_4]$ that the n.m.r. coalescence point could be approached at low temperatures. Subsequently, a vibrational analysis of the paramagnetic molecule

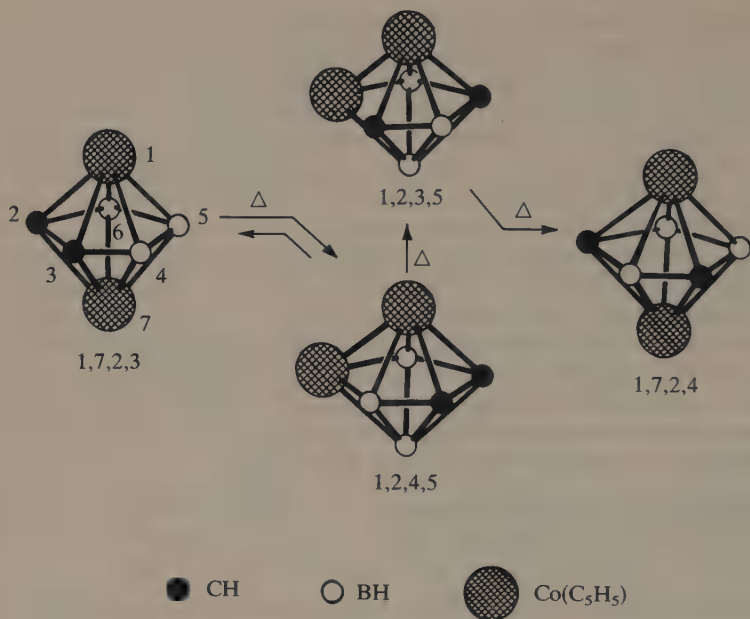
^{5(a)} T. J. Marks and J. R. Kolb, *J. Amer. Chem. Soc.*, 1975, **97**, 27; (b) T. J. Marks and W. J. Kennelly, *J. Amer. Chem. Soc.*, 1975, **97**, 1439; (c) H. D. Empsall, E. Mentzer, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 861.

$[(C_5H_5)_2VBH_4]^{5b}$ indicated considerable covalency in the V—H(BH₄) bonds. At $-90^\circ C$, the fluxionality of this molecule was arrested; resonances due to bridge and terminal hydrogens were evident below this temperature. A free energy of activation of $7.6 \pm 0.3 \text{ kcal mol}^{-1}$ compares with a barrier of $ca. 5.0 \pm 0.6 \text{ kcal mol}^{-1}$ estimated for $[(C_5H_5)_3UBH_4]$. The small size of these barriers emphasizes the facility of the intramolecular rearrangement which may well involve a bidentate–terdentate conversion. In view of the above results, the iridium and rhodium complexes $[IrH_2(BH_4)L_2]$ (L = PBu_2^tMe , PBu_3^t , $PBu_2^tBu^n$, or PBu_2^tPh), prepared from $[IrHCl_2L_2]$ by treatment with sodium borohydride, are remarkable.^{5c} These compounds all exhibit typical i.r. spectra for doubly bridged metal–BH₄ bonding but are non-fluxional in solution with resonances at $ca. \delta = -6.5$ for bridging $[IrH_2B]$ and at $\delta = 6.8\text{--}7.8$ for terminal BH₂ protons. Perhaps the bulky phosphines prevent the attachment of a third BH₄ hydrogen in the intermediate $[IrH_3BH]$ species necessary for the bridge–terminal exchange. It should be noted that, despite the obvious difference in structural types, the terminal protons in static $[(C_5H_5)_2VBH_4]$ and $[IrH_2(BH_4)L_2]$ resonate at lower field than the bridging hydrogens.

Carboranes and Metallocarboranes.—This is one of the most active areas of inorganic research and a great deal of interesting work is published each year. A small number of topics have been singled out for specific mention.

Intramolecular Rearrangements. The facile intramolecular rearrangement of borane, carborane, and metallocarborane molecules is amply documented. Mechanistic understanding of these processes, many of which have no precedent in other areas of chemistry, is, however, in its infancy. An important paper, which complements earlier work by Hawthorne and co-workers on large cages,^{6a,b} may provide an initial basis for rationalizing thermal isomerization processes for small metallocarboranes.^{6c} Thermolysis of $[1,2,4-(\eta-C_5H_5)CoC_2B_3H_5]$ produced no isomerization to the 1,2,3- or 1,2,6-systems.^{6c} The seven-vertex cage $[1,2,3-(\eta-C_5H_5)CoC_2B_4H_6]$ however, isomerized in high yield at $400^\circ C$ to the 1,2,4-isomer. Rearrangement of $[1,7,2,3-(\eta-C_5H_5)_2Co_2C_2B_3H_5]$ occurred stepwise, yielding $[1,7,2,4-(\eta-C_5H_5)_2Co_2C_2B_3H_5]$ via the intermediate 1,2,4,5- and 1,2,3,5-isomers as shown in Scheme 1. While it should be remembered that the isolation of intermediates does not *prove* a reaction mechanism, the formation of all three sequential products in this reaction can be accommodated if (a) atoms permute by a triangular rotation on the polyhedron surface [as opposed to a less likely diamond–square–diamond (dsd) mechanism], (b) carbon atoms may not move from a low to a high (apex) co-ordination position, (c) carbon atoms will not decrease their mutual separations, (d) rotation of B₂C or B₂Co triangles is preferred, and (e) the metal atom prefers an apex position provided that rules (b)–(d) are followed. It is clear, at least for $[(\eta-C_5H_5)_2Co_2C_2B_3H_5]$, that cobalt is *not* restricted to positions of high co-ordination number (*cf.* 1,2,4,5- and 1,7,2,3-isomers), although for cages with ≥ 6 boron atoms such a restriction has generally been operative.^{6a,b} {Note, however,

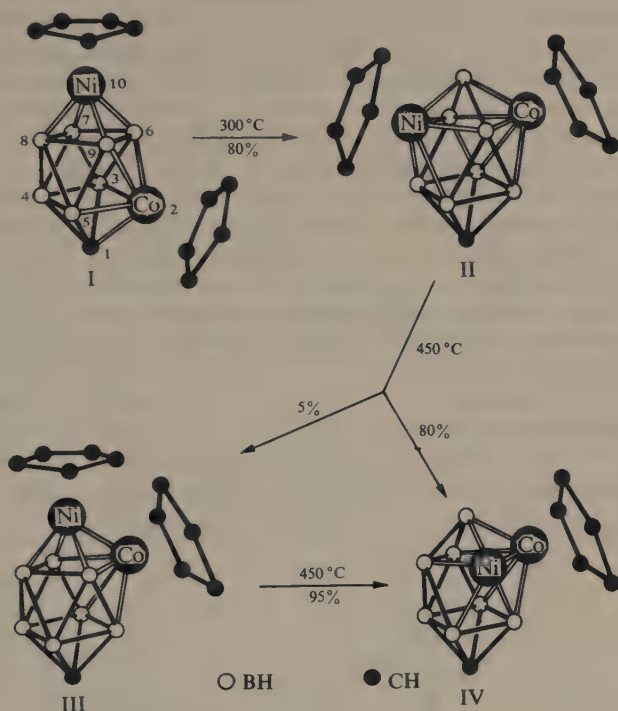
⁶ (a) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1974, **96**, 3085; (b) M. F. Hawthorne, K. P. Callahan, and R. J. Wiersema, *Tetrahedron*, 1974, **30**, 1795; (c) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 1975, **97**, 4213; (d) G. D. Mercer, M. Tribo, and F. R. Scholer, *Inorg. Chem.*, 1975, **14**, 764; (e) C. G. Salentine and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1975, **97**, 6382; (f) B. J. Meneghelli and R. W. Rudolph, *Inorg. Chem.*, 1975, **14**, 1429.



Scheme 1

that $[1,2,4-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CMe}_2)_2\text{B}_8\text{H}_8]$ is converted into $[1,2,3-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CMe}_2)_2\text{B}_8\text{H}_8]$ via $[10,2,3-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CMe}_2)_2\text{B}_8\text{H}_8]^{6d}$ and that $[2,10,1-(\eta\text{-C}_5\text{H}_5)_2\text{CoNiCB}_7\text{H}_8]$ and $[6,10,1-(\eta\text{-C}_5\text{H}_5)_2\text{CoNiCB}_7\text{H}_8]^{6e}$ contain nickel atoms in low-co-ordinate vertices.} Grimes^{6c} suggests that while the driving force for the $1,7,2,3 \rightarrow 1,7,2,4$ conversion is the separation of carbon atoms, strong cobalt–cobalt bonding lowers the activation energy for apex \rightarrow equatorial migration of cobalt, thus allowing a facile reaction path via a series of trigonal rotations. Pyrolysis of the eight-vertex cobaltacarboranes $[3,1,7-(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_5\text{H}_7]$ and $[3,5,1,7-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_4\text{H}_6]$ resulted in considerable cage fragmentation (boron and cobalt transfer) but no isomerization to the $[3,1,8-(\eta\text{-C}_5\text{H}_5)_2\text{CoC}_2\text{B}_5\text{H}_7]$ or $[3,5,2,8-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_4\text{H}_6]$ isomers predicted if the number of Co–C bonds was to be minimized. If the structures of these compounds have been correctly assigned (no X-ray data are available) these results may imply that the thermal stabilities of the 3,1,7-monocobalt and 3,5,2,8-dicobalt cages are higher than those of any other isomer. Alternatively, there may be a kinetic barrier to interconversion.

Conversion of the nine-vertex cage $[1,7,5,6-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7]$, in which two cobalt atoms are adjacent, into the isomer $[1,8,5,6-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7]$ produced an equilibrium, the first such example for *closo*-metallo-carboranes. The ΔH for the $1,8,5,6 \rightarrow 1,7,5,6$ process is -2 kcal mol^{-1} , perhaps indicating a fine balance between competing steric and electrostatic repulsion effects on the one hand and strong cobalt–cobalt bonding on the other.



Scheme 2

A second important paper this year on polyhedral rearrangements deals with the synthesis and thermal isomerization of the mixed-metal bimetallocarbaborane $[(C_5H_5)_2CoNiCB_7H_8]$ (Scheme 2).^{6e} The presence of a direct nickel-cobalt bond in the thermally most stable $[6,9,1-(\eta-C_5H_5)_2CoNiCB_7H_8]$ isomer IV and preference of nickel for a high-co-ordinate position in IV was established, although nickel atoms in I and III occupy low-co-ordinate sites. Rearrangement processes were discussed in terms of the dsd mechanism (*cf.* ref. 6c).

This year's work thus establishes clearly that in metallocarbaboranes of intermediate stability the presence of metal atoms in low-co-ordinate positions is not precluded. Furthermore, strong metal-metal bonds are possible and may play an important role in determining relative stabilities for other di- and polymetallocarbaboranes. Rearrangements of metallocarbaboranes incorporating second- and third-row transition elements will be interesting in this regard. It is also clear that a definitive experiment to distinguish between the alternative dsd and trigonal-rotational mechanisms for metallocarbaborane interconversion has not yet been described.

The reduction of *closo*-carbaborane cages, with subsequent cage-opening and insertion of a metal ion into the vacant site, is a valuable synthetic route to metallocarbaborane complexes. The mechanisms of ring-opening are generally obscure. Evidence is, however, accumulating that two-electron reduction of *closo*-carbaboranes occurs *via* conversion of deltahedra to *nido* counterparts. Thus extended Hückel MO calculations confirm that $D_{3h}[C_2B_3H_5]^{2-}$ should not be stable and that trigonal-bipyramidal isomers are energetically inaccessible.^{6f} However, square-pyramidal isomers of $[C_2B_3H_5]^{2-}$ have appreciably higher stabilities, with the stability order *trans*-basal-basal > *cis*-basal-basal > apical-basal. Accessible and symmetry-allowed interconversion pathways between these three isomers are available (Figure 1). Addition of two protons to give $C_2B_3H_7$ changes the relative stability ordering to apical-basal > *trans*-basal-basal > *cis*-basal-basal, such that the two hydrogens can be accommodated in bridging positions on non-trigonal faces of the apical-basal isomer. The known isomer of $C_2B_3H_7$ (isoelectronic with $[C_2B_3H_5]^{2-}$) has this stereochemistry. For the six-vertex carbaborane anions $[C_2B_4H_6]^{2-}$ derived from $C_2B_4H_6$, all pentagonal-bipyramidal isomers are more stable than octahedral species. Hence, open, pyramidal forms of $[C_2B_3H_5]^{2-}$ and $[C_2B_4H_6]^{2-}$ appear favoured over their *closo* analogues. The rearrangements *closo* $\xrightleftharpoons[-2e]{+2e}$ *nido* and *nido* $\xrightleftharpoons[-2e]{+2e}$ *arachno* provide a rationale for polyhedral expansion. Metal fragments capable of accomplishing these conversions can be predicted.^{4d,e}

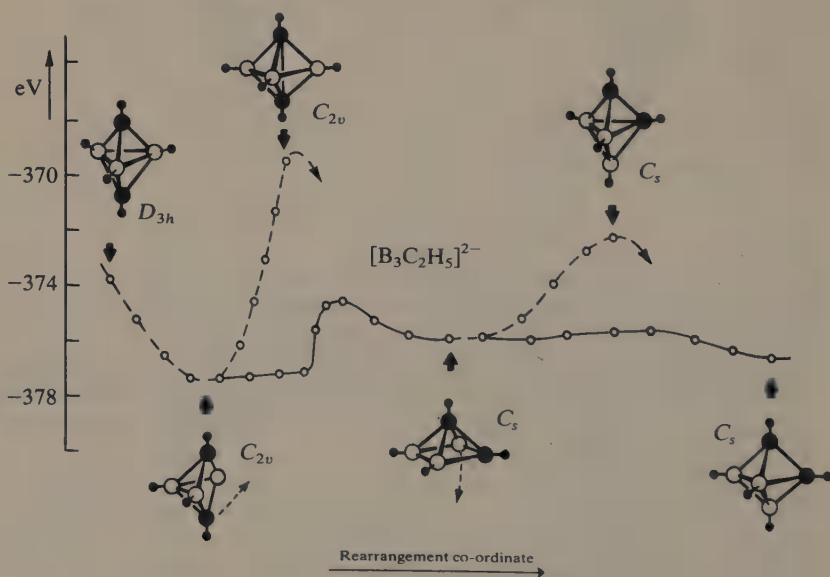
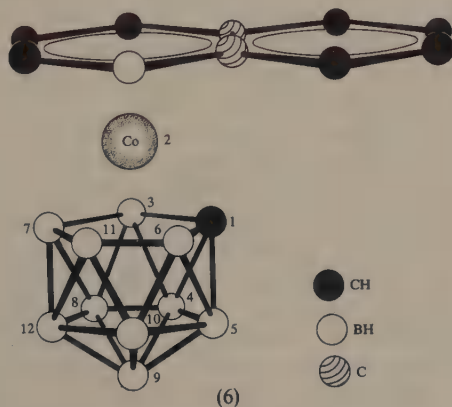


Figure Energy as a function of geometry for $[C_2B_3H_5]^{2-}$. The solid line represents the interconversion of isomeric forms of $[C_2B_3H_5]^{2-}$ via symmetry-allowed arcing movements of the designated atoms. The broken line designates interconversion via a disd mechanism (Reproduced by permission from *Inorg. Chem.*, 1975, **14**, 1429)

Synthesis. There has been very little information relating to the mechanism of formation of carbaboranes. The kinetics of formation of derivatives of 1,2-dicarbapcloso-dodecaborane(12), from $B_{10}H_{12}(Me_2S)_2$ and acetylenes $RC\equiv CH$, show that the rate determining process is attack by the acetylene on $B_{10}H_{12}(Me_2S)$ forming the adduct $B_{10}H_{12}(Me_2S)(RC\equiv CH)$. Subsequent loss of a molecule of Me_2S from B-9, and co-ordination of the acetylene to B-9, adjacent to B-10, yields a geometry favourable to *closo*-carbaborane formation.^{7a}

Importantly, isolable $B_{10}H_{12}L$ species synthesized by other workers are *not* intermediates and hence not identical to the active species $B_{10}H_{12}L$ formed *in situ* by reversible dissociation of $B_{10}H_{12}L_2$. Clearly positive identification of these active species which may also be implicated in $[B_{10}H_{10}]^{2-}$ formation is desirable.

The general synthetic methods, namely cage expansion by carbaborane reduction in the presence of metal halide and sodium cyclopentadienide, direct insertion of metal fragments (e.g. d^{10} complexes) into a polyhedral cage and the polyhedral subrogation reaction, have been described in detail in previous *Annual Reports* and recent surveys.^{7b,c} These methods have been extended this year. Only a few novel examples can be mentioned. Until this year the only π -hydrocarbon ligand which had been extensively utilized as a capping ligand in metallocarbaboranes was $C_5H_5^-$. Derivatives with $\eta^8-C_8H_8$ ^{7d} and $\eta^6-C_{10}H_8$ ^{6e} have now been synthesized. Thus reaction of $[(C_8H_8)TiCl]_2$ with $Na_2C_2B_9H_{11}$ followed by treatment with Et_4N^+ yielded $[Et_4N][3,1,2-(\eta^8-C_8H_8)TiC_2B_9H_{11}]$. Reaction with H_2O_2 gave $[3,1,2-(\eta^8-C_8H_8)TiC_2B_9H_{11}]$.^{7d} Reaction of $[2,1-(\eta^5-C_5H_5)CoCB_{10}H_{11}]$ with sodium naphthalide followed by treatment with $C_5H_5^-$ and Co^{II} gave orange, diamagnetic $[2,1-(\eta^6-C_{10}H_8)CoCB_{10}H_{11}]$, formulated as (6) {cf. $[(C_{10}H_8)Cr(CO)_3]$ } and the first metallocarbaborane with a neutral η^6 -arene ligand.^{6e} There are other metallocarbaborane complexes purported to contain η^2 - and η^4 -arene ligands in the recent literature but these must be considered highly speculative. In view of the interest and

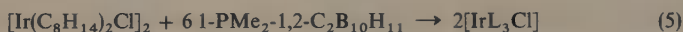


⁷ (a) W. E. Hill, F. A. Johnson, and R. W. Novak, *Inorg. Chem.*, 1975, **14**, 1244; (b) M. F. Hawthorne, *J. Organometallic Chem.*, 1975, **100**, 97; (c) F. G. A. Stone, *J. Organometallic Chem.*, 1975, **100**, 257; (d) C. G. Salentine and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1975, 848; (e) C. G. Salentine and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1975, **97**, 426; (f) F. Y. Yo, C. E. Strouse, K. P. Callahan, C. B. Knobler, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1975, **97**, 428; (g) P. L. Timms, *Angew. Chem. Internat. Edn.*, 1975, **14**, 2/3; (h) E. L. Hoel and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1975, **97**, 6388.

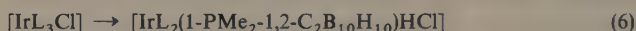
controversy surrounding the structures of 'titanocenes' and related complexes the characterization of $[\text{Me}_4\text{N}]_2[[1,6\text{-C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2]_2\text{Ti}]$ as a 14-electron titanacarborane is notable.^{7e,f} From the few studies presently available it appears that metallocarborane complexes of the early transition metals are considerably more stable than the corresponding cyclopentadienyl complexes. Whether these metallocarboranes undergo the facile thermal rearrangements typical of the cyclopentadienyl titanium complexes remain to be established.

The use of metal vapours in the cage expansion of carbaboranes is a potentially useful but, to date, little used synthetic method. Thus, nickel vapour reacts with the *closo*-carbaborane $\text{C}_2\text{B}_9\text{H}_{11}$ to give the known complex $[(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Ni}]$ derived from the *nido*-anion $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$.^{7g}

A variety of *B*- σ -carbaboranyl complexes of iridium have been obtained by oxidative addition of terminal B—H bonds to iridium(I) species^{7h} [equations (5) and (6)].



(L)



(7)

The complex (7) has a *cis*-octahedral stereochemistry at iridium with three phosphorous atoms *cis* to the hydride and the chloride *trans*. The carbaborane cage is probably attached to the metal *via* a boron atom in the 3- or 6-position. Intermolecular oxidative addition is also possible. Thus reaction of $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ with $[(\text{Ph}_3\text{P})_3\text{IrCl}]$ gave small amounts of $3\text{-}[(\text{PPh}_3)_2\text{IrHCl}]\text{-1 2-C}_2\text{B}_{10}\text{H}_{11}$. Substitution on the cage was at the 3,6-sites. These reactions thus complement the methods discussed in last year's Report for synthesizing *B*- σ -carbaboranyl complexes.

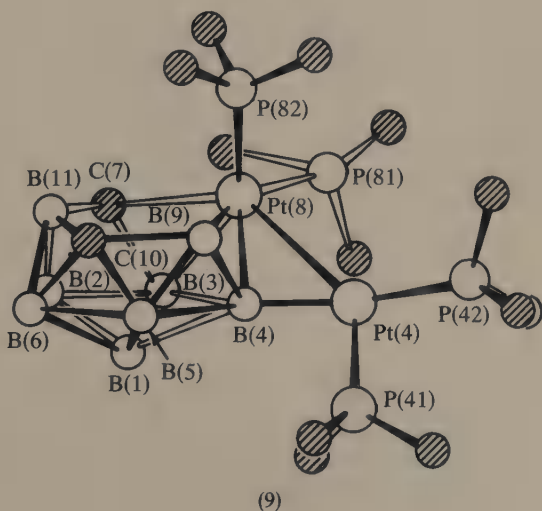
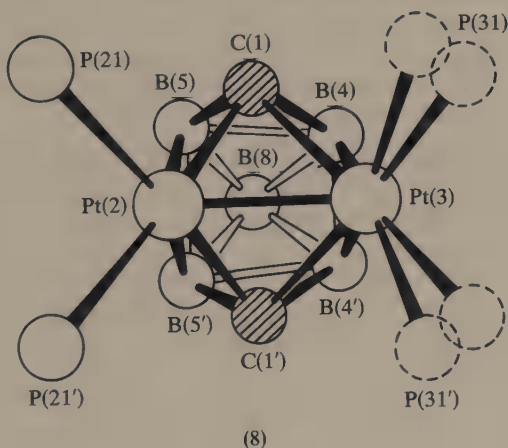
Structures of Carbaboranes and Metallocarboranes. With the availability of automated diffractometers, X-ray analysis has become a rapid analytical tool, not least in the field of metallocarboranes. Structures are too numerous to list. We mention only a few important structural trends.

X-ray data are now available for a wide variety of twelve-vertex metallocarboranes in which the metal *d*-electron configurations vary from d^2 to d^9 . Electron-rich d^8 and d^9 complexes, e.g. $[(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2\text{Ni}^{II}]^{2-}$, have 'slipped' sandwich structures with the distortion largest in the d^9 cases. For electron-deficient metallocarboranes, of which the 15-electron complex $\text{Cs}\{[\text{C}_2\text{B}_9\text{H}_9\text{Me}_2]_2\text{Cr}\}$ is an example, a symmetrical structure with long metal-ring distances is observed. Long metal-ring bonds are also evident in the 14-electron 13-vertex cage complex $[\text{Me}_4\text{N}]_2[[1,6\text{-C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2]_2\text{Ti}]$. An alternative explanation of the slippage in the electron-rich species has now been proposed.^{8a} Basically, comparison with the MO energy-level diagram of ferrocene is useful. In the bis-dicarbollide systems the orbitals corresponding to the $2e_{1g}$ MO's of ferrocene are antibonding with respect to

^a (a) P. A. Wegner, *Inorg. Chem.*, 1975, **14**, 212; (b) W. T. Robinson and R. N. Grimes, *Inorg. Chem.*, 1975, **14**, 3056; (c) G. K. Barker, M. Green, J. L. Spencer, F. G. A. Stone, B. F. Taylor, and A. J. Welch, *J.C.S. Chem. Comm.*, 1975, 804; (d) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1975, **97**, 296.

both the metal–ring interactions and the icosahedral cage framework. In d^8 and d^9 complexes, two and three electrons occupy these antibonding MO's. Distortion and eventually cage-opening (*closo*→*nido*) ensue. The process is analogous to that occurring on reduction of *closo*- $C_2B_{10}H_{12}$ systems. Although the author mentions that similar distortions do *not* occur for electron-rich $[(C_5H_5)_2M]$ complexes, it should be pointed that there are some unusual features in the structure of gaseous nickelocene (a 20-electron complex), in particular that the Ni–C bonds may not all be equivalent.

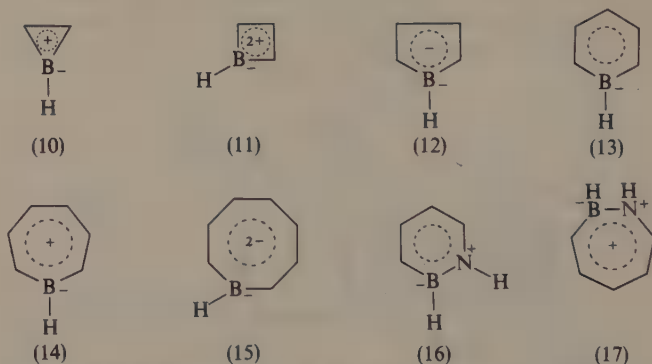
The structure of $[2\text{-Me-}1,7,2,4\text{-(}\eta\text{-}C_5H_5)_2Co_2C_2B_3H_4]$ consists of a triple-decked sandwich, analogous to the $[(\eta\text{-}C_5H_5)_3Ni_2]^+$ ion. The planar $[C_2B_3H_5]^{4-}$ ring system in 1,7,2,3- and 1,7,2,4- $[(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5]$ is isoelectronic and isostructural with $[C_5H_5]^-$. Development of metallocene-like polymers based on $[C_2B_3H_5]^{4-}$ thus seem possible.^{8b}



The reactions of *closo*-2,4- $\text{C}_2\text{B}_5\text{H}_7$ and *closo*-1,6- $\text{C}_2\text{B}_8\text{H}_{10}$ with $[\text{Pt}(\text{styrene})(\text{PEt}_3)_2]$ and $[\text{Pt}(\text{C}_8\text{H}_{12})(\text{PMe}_3)_2]$ respectively afforded the novel complexes (8) and (9).^{8c} Compound (8) has a closed nine-atom bimetallocarbaborane structure but illustrates that M—M bonds in metallocarbaboranes can be very weak. The Pt—Pt bond length of 3.051(4) Å is barely a bonding distance. In (9) an unusual exocyclic Pt—Pt bond is present which can readily be removed to generate *nido*-[8,8- $\{(\text{Me}_3\text{P})_2\}$ -7,8,10-CPtCB $_8\text{H}_{10}$]. Despite much effort it does not yet seem possible to predict the course of these d^{10} insertions. It is also becoming obvious (*cf.* refs. 6c and 6e) that metal-metal bonds in metallocarbaboranes can vary enormously in strength.

The frequent occurrence of unusual structures in the products derived from insertion of electron-rich metal fragments into carbaborane cages should not mask the utility of electron-counting rules for rationalizing the basic polyhedral geometries of metallocarbaboranes. For example the structure of $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{C}_2\text{B}_6\text{H}_8]$ is that of a capped, tricapped, trigonal prism and differs from the idealized bicapped square antiprism of other ten-vertex borane species. However, this molecule does not have the 22 electrons required for skeletal bonding according to the $2n+2$ rule.^{4d,e} With 20 electrons only, $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{C}_2\text{B}_6\text{H}_8]$ should be derived from a nine-vertex polyhedron, as is observed.^{8d}

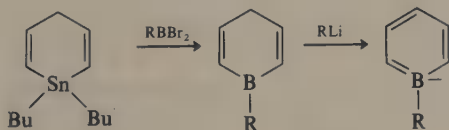
Boracarbocycles and Their Metal Complexes.—The search for carbocycles with aromaticity, as predicted by the Hückel $4n+2$ rule, together with the notable stabilization of reactive molecules which can often be achieved by attachment to a suitable transition-metal fragment, has motivated much research on metal-hydrocarbon π -complexes. The isoelectronic character of CH and BH^- and C—C and B—N units is well recognized and has been exploited in the developing chemistry of carbaboranes and borazines. Substitution of B—H[−] or B—N for C—H fragments in $(4n+2)\pi$ carbocycles gives rise to boracarbocycles (10)—(15) or borazacarbocycles [*e.g.* (16)—(17)]. Although derivatives of a few of these are known [*e.g.* pentaphenylborole corresponding to the polyene of (12)^{9a} and



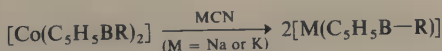
⁹ (a) J. J. J. Eisch, H. K. Hota, and S. Kozima, *J. Amer. Chem. Soc.*, 1969, **91**, 4575; (b) M. F. Lappert in 'The Chemistry of Boron and its Compounds', ed. E. L. Muetterties, Wiley, New York, 1968, Ch. 6; (c) A. J. Ashe, *tert.*, E. Myers, P. Shu, T. V. Lehmann, and J. Bastide, *J. Amer. Chem. Soc.*, 1975, **97**, 6865; (d) G. E. Herberich and H. J. Becker, *Angew. Chem. Internat. Edn.*, 1975, **14**, 184; (e) G. E. Herberich, G. Greiss, and H. F. Heil, *Angew. Chem. Internat. Edn.*, 1970, **9**, 805; (f) R. N. Leyden and M. F. Hawthorne, *Inorg. Chem.*, 1975, **14**, 2018; (g) G. E. Herberich, H. J. Becker, and G. Greiss, *Chem. Ber.*, 1974, **107**, 3780; (h) J. J. Eisch and J. E. Galle, *J. Amer. Chem. Soc.*, 1975, **97**, 4436.

borazaronaphthalenes related to (16)^{9b}], synthesis of other boracarbocycles has been very limited. Recently, two groups^{9c,d} have characterized phenylborinate (borabenzene) anions by two different routes (Scheme 3). Ashe and co-workers have also made alkyl- and bromo-substituted anions. The anions are pyrophoric. Originally the phenylborinate anion was trapped as the $[(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_5\text{H}_5\text{BPh})\text{Co}]^+$, $[(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_5\text{H}_5\text{BPh})\text{Co}]$, or $[(\eta^5\text{-C}_5\text{H}_5\text{Ph})_2\text{Co}]$ complexes by ring expansion of $\eta^5\text{-C}_5\text{H}_5$ rings of cobaltocene with phenylboron dichloride.^{9e} A dicarbollylphenylborinate-cobalt complex $[3,1,2\text{-}\{1\text{-C}_6\text{H}_5(\eta^6\text{-C}_5\text{BH}_5)\}\text{CoC}_2\text{B}_9\text{H}_{11}]$ has been prepared in analogous fashion.^{9f} For the synthesis of other transition-metal derivatives, ligand transfer from the cobalt complexes can be used (*cf.* transfer of cyclobutadienes), but prior generation of the anion would seem preferable. The 6π -aromatic system (13) can be compared to the cyclopentadienide ion. Indeed the air-stable bis(borabenzene)iron complexes^{9c,g} appear to resemble ferrocene quite closely. In particular, the chemical isomer shift, δ , is identical (0.72 mm s^{-1}) to that of ferrocene, indicating that differences in σ -, π -, and δ -components to the bonding, if any, compensate one another so that no net change in s -electron density at the nucleus is apparent. A comparison of δ and Δ values with those of the known isoelectronic $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Fe}]^{2+}$ species would be rewarding. The bis(borabenzene)iron complexes also undergo electrophilic substitution; a monoacetyl derivative has been characterized.^{9c} Ferrocene is, however, approximately four times more reactive than bis-(1-methylborabenzene)iron. Although the borabenzene ring is bis-(1-methoxyborinato)cobalt is asymmetrically bonded to the metal atom with substantially longer Co—B than Co—C bond lengths, it must be remembered that the cobalt complex is formally a 19 electron species; a distortion might therefore be expected. An X-ray structure of the corresponding iron complex will be interesting.

In view of the stability of these systems it seems clear that attempts to generate complexes derived from other boracarbocycles may well be feasible. In this context, the recent synthesis of heptaphenylborepin (18) by a suprafacial sigmatropic rearrangement of heptaphenyl-7-borabicyclo[2,2,1]heptadiene, followed by a disrotatory ring-opening of the bicyclic intermediate, is of interest.^{9h} The borepin (18) with six π -electrons may well be planar and aromatic; spectra of (18) compare well with spectra of the heptaphenyltropenium ion. Nevertheless, corroborative X-ray data seem necessary, especially in view of the propensity of other seven-membered heterocycles to undergo valence tautomerism. Diene, triene, or boratrienyl complexes of (18) seem possible. The electron deficiency of boron could also be satisfied by a metal lone pair, with interesting stereochemical consequences.

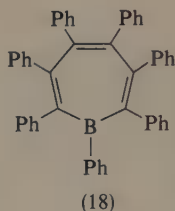


Ref. 9c



Ref. 9d

Scheme 3



Boron-Carbon π -Bonding in Vinylboranes.—Last year's Report (p. 193) mentioned briefly evidence for B—C π -bonding in vinylboranes. Spectroscopic support for electron delocalization in vinylboranes has now been summarized.^{10a} Unfortunately, previous assessments of B—C bond shortening have been hampered by a lack of accurate structural data. The gas-phase structure of trivinylborane has now been determined.^{10b} The molecule is dynamic, having a planar BC_3 skeleton but with extreme thermal motion of the vinyl groups. The B—C bond length of 1.558(3) Å is shorter, at the 4σ level, than the B—C bond length in triphenylborane [1.577(5) Å av]. Comparison of these distances is valid since both compounds have $\text{B}_{sp^2}\text{—C}_{sp^2}$ links. The inference of B—C π -bonding appears justified although the extent of bond shortening *per vinyl group* is slight. Carbon-13 n.m.r. data have been interpreted as indicating that electron drift from carbon to boron is maximized in the monovinylboranes, despite the presence of competing π -donors on boron.^{10a} In view of the predicted strongly mesomeric π -donor properties of fluorine in species such as H_2BF ,^{1c} it seems unusual that B—C π -bonding should fall off in the sequence $\text{F}_2\text{B}(\text{C}_2\text{H}_3) > \text{FB}(\text{C}_2\text{H}_3) > \text{B}(\text{C}_2\text{H}_3)_3$. Indeed *ab initio* studies show that the absolute charge on C_α of the vinylboranes $\text{F}_x\text{B}(\text{C}_2\text{H}_3)_{3-x}$ decreases with increased vinylation.^{10c} Delocalization of vinyl π -density is thus greatest in trivinylborane. It is unfortunate that structural data for $\text{F}_2\text{B}(\text{C}_2\text{H}_3)$ ^{10d} are not sufficiently accurate to allow a comparison with $\text{B}(\text{C}_2\text{H}_3)_3$. Comparison of calculations for vinyl- and methyl-boranes shows that a vinyl group donates more than twice as much π -density to boron in $\text{F}_2\text{B}(\text{C}_2\text{H}_3)$, $\text{FB}(\text{C}_2\text{H}_3)_2$, or $\text{B}(\text{C}_2\text{H}_3)_3$ than a methyl group in F_2BMe , FBMe_2 , or BMe_3 . Hence B—C ($p_\pi\text{—}p_\pi$) interactions in vinylboranes are considerably more important than hyperconjugation in methylboranes.

Boron Halides.—The extent of B—X ($p_\pi\text{—}p_\pi$) bonding in the boron halides has intrigued inorganic chemists for years and is directly pertinent to discussion of relative Lewis acidities. An attractive approach to this problem would be comparison of structural and spectroscopic properties of the mixed halides $\text{BX}_n^1\text{X}_{3-n}^2$ where competitive B—X¹ and B—X² $p_\pi\text{—}p_\pi$ interactions might be expected. Unfortunately the pure mixed halides are not isolable. Despite this an elegant study^{11a} has recently shown that from a statistical equilibrium mixture of $\text{BCl}_n\text{F}_{3-n}$ ($n = 0\text{—}3$), photoelectron and microwave spectra of individual species can be obtained. For example, for BClF_2 , IP's of 12.85 ($4b_2$), 13.00 ($2b_1$), 15.1 ($5a_1$), 16.93 ($3b_2$, a_2), and 18.35 ($1b_1$) eV were experimentally observed. Ionization from $4a_1$ (calc. 18.58 eV) and

¹⁰ (a) L. W. Hall, J. D. Odom, and P. D. Ellis, *J. Amer. Chem. Soc.*, 1975, **97**, 4257; (b) A. Foord, B. Beagley, W. Reade, and I. A. Steer, *J. Mol. Structure*, 1975, **24**, 131; (c) N. J. Fitzpatrick and N. J. Mathews, *J. Organometallic Chem.*, 1975, **94**, 1; (d) J. R. Durig, R. O. Carter, and J. D. Odom, *Inorg. Chem.*, 1975, **13**, 701.

$2b_2$ (calc. 19.32 eV) was not detected. A B—Cl bond length of 1.71(1) Å and an FBF angle of 116.6(1)° were derived from the microwave spectrum of this compound. The B—Cl bond has 14% π -character; *ab initio* calculations agree with this estimate and indicate that the $B2p_\pi$ — $Cl3p_\pi$ overlap population is greater than $B2p_\pi$ — $F2p_\pi$. This result agrees with earlier EHMO calculations on the trihalides BX_3 where π -charge transfer from halogen to boron decreased in the order $BI_3 > BBr_3 > BCl_3 > BF_3$ although the σ -charge drift $X \rightarrow B$ dominates contributions to the overall bond polarity.^{11b} This opinion is not shared universally, however. The *a priori* prediction of a more compatible p_π — p_π overlap in the B—F bond has usually led to the text book inference of greatest π -bond order in the fluoride. This view still persists.^{10a} Nevertheless the order of π -back-donation from ligand to boron $B-N > B-S \approx B-I > B-O \approx B-Br > B-Cl > B-F$ deduced earlier seems realistic and can be compared with $B-N > B-O > B-F$ calculated for H_2BX species.^{1c}

While halogen bridging is common for the heavier Group III metal halides it is rare in boron chemistry. At very low temperatures (−155 °C) 1 : 1 mixtures of BF_3 and $[Bu^4N]^+[BF_4]^-$ give ^{19}F n.m.r. spectra consisting of a high-field doublet (J_{FBF} 95 ± 10 Hz) and a broad low-field resonance with area ratios of 1 : 6 consistent with the presence of the very labile single-fluorine-bridged species $[B_2F_7]^-$, the first time this ion has been observed in solution.^{11d}

The Boron–Phosphorus Bond.—The nature of the co-ordinate bond between boron and phosphorus in simple co-ordination compounds has been a source of considerable controversy. Some of the more puzzling aspects, which appear to have largely defied logical explanation to date, are the variations in P—B bond lengths which accompany changes in the substituents on boron and phosphorus together with some rather unusual stability sequences. Thus H_3P, BH_3 and F_3P, BH_3 have P—B bond lengths [1.937(5) and 1.836(6) Å] near the extremes for borane (BH_3) adducts yet these compounds are considerably less stable than HF_2P, BH_3 [B—P, 1.832(9) Å], Me_3P, BH_3 [B—P, 1.901(7) Å], or HMe_2P, BH_3 [B—P, 1.906(6) Å]. The P—B bond lengths of 1.921(7) Å and 1.84(2) Å recently determined for H_3P, BH_3 ^{12a} and $MePF_2, BH_3$ ^{12b} respectively, the former a compound of low dissociative stability, shed no further light on this matter. The most that can be said at present is that for BH_3 adducts the B—P bond lengths lie in two groups, with B—P bonds in fluorophosphine adducts ca. 0.06 Å shorter than in the phosphine and methylphosphine series.

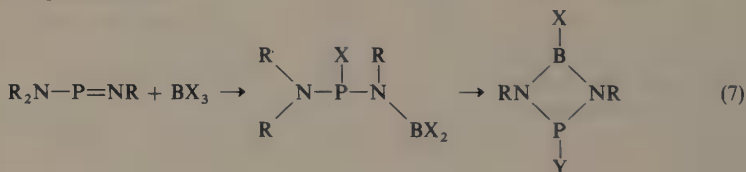
For boron trihalide complexes the situation is clearer. Crystal structures have been determined for Me_3P, BX_3 ($X = Cl, Br, \text{ or } I$) this year.^{12c} Boron–phosphorus bond lengths are 1.957(5) Å ($X = Cl$), 1.924(12) Å ($X = Br$), and 1.918(15) Å ($X = I$). There is a significantly shorter B—P bond in the chloride complex compared with the bromide or iodide. Thus the pattern of donor–acceptor bond strengths, and

¹¹ (a) H. W. Kroto, M. F. Lappert, M. Maier, J. B. Pedley, and M. Vidal, *J.C.S. Chem. Comm.*, 1975, 810; (b) M. F. Lappert, M. R. Litzow, J. B. Pedley, P. N. K. Riley, and A. Tweedale, *J. Chem. Soc. (A)*, 1968, 3105; (c) M. F. Lappert, M. R. Litzow, J. B. Pedley, P. N. K. Riley, T. R. Spalding, and A. Tweedale, *J. Chem. Soc. (A)*, 1970, 2320; (d) J. S. Hartman and P. Stilbs, *J.C.S. Chem. Comm.*, 1975, 566.

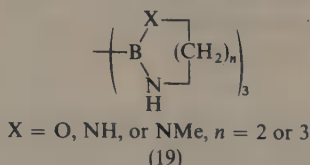
¹² (a) J. D. Odom, V. F. Kalasinsky, and J. R. Durig, *Inorg. Chem.*, 1975, **14**, 2837; (b) R. A. Cresswell, R. A. Elzaro, and R. H. Schwendeman, *Inorg. Chem.*, 1975, **14**, 2256; (c) D. L. Black and R. C. Taylor, *Acta Cryst.*, 1975, **B31**, 1116; (d) D. C. Mente and J. L. Mills, *Inorg. Chem.*, 1975, **14**, 1862; (e) P. Cassoux, R. L. Kuczkowski, P. S. Bryan, and R. C. Taylor, *Inorg. Chem.*, 1975, **14**, 126; (f) P. M. Kuznesof, F. B. T. Pessine, R. E. Burns, and D. F. Shriver, *Inorg. Chim. Acta*, 1975, **14**, 271.

possibly Lewis acidities, evident in the $\text{Me}_3\text{N}, \text{BX}_3$ and MeCN, BX_3 series is followed with $\text{BI}_3 \geq \text{BBr}_3 > \text{BCl}_3$. This order receives direct support from gas-phase calorimetric measurements.^{12d} Furthermore the B—P bond length in $\text{Me}_3\text{P}, \text{BH}_3$ [1.901(7) Å] is *shorter* than in any of the halide complexes $\text{Me}_3\text{P}, \text{BX}_3$ whereas for $\text{Me}_3\text{N}, \text{BX}_3$ (X = H, Cl, NF) the distances are virtually identical.^{12e} The B—N bond length in $\text{Me}_3\text{N}, \text{BH}_3$ [1.638(10) Å] is longer than in $\text{Me}_3\text{N}, \text{BX}_3$ (X = Br or I). Thus, the greater affinity of BH_3 than the boron halides towards phosphine donors, predicted chemically, seems substantiated. CNDO-2D calculations of dipole moments for $\text{Me}_x\text{H}_{3-x}\text{E}$ and $\text{Me}_x\text{H}_{3-x}\text{E}, \text{BH}_3$ (E = N or P; $x = 0-3$) provide evidence for substantial differences in B—N and B—P bonds in these simple adducts.^{12f} Co-ordination of NH_3 to BH_3 results in charge transfer primarily between N-bound and H-bound hydrogens (0.33e) but for phosphine complexes the transfer is largely from phosphorus to boron (0.27e). Whereas the B—N bonding MO remains essentially unchanged on methyl substitution (46% covalent character in the B—N bond with essentially $sp^{2.8}$ hybridization at nitrogen), substantial changes in hybridization at phosphorus (from $sp^{1.3}$ in PH_3, BH_3 to $sp^{1.7}$ in $\text{Me}_3\text{P}, \text{HB}_3$) occur on formation of B—P bonds. The B—P bond has considerably more covalent character (61%) and a higher *s*-character. It also appears from these calculations that distortion of the lone-pair electrons of Me_3P and PH_3 by BH_3 is more favourable for the former ligand.

The Boron–Nitrogen Bond.—Research in boron–nitrogen chemistry is focused to a large extent on compounds where B—N π -bonding plays a major role. This year synthetic methods have been developed for several molecules whose ground-state properties should be interesting. Thus the first 1,3,2,4-diazaboretidines have been synthesized [equation (7)].^{13a}

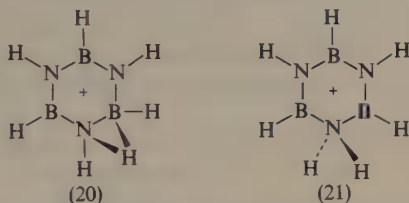


Convenient routes to dialkylaminohydridophenoxyboranes have been described.^{13b} Restricted rotation about B—N bonds in these molecules is expected and experimentally observable by means of n.m.r. Aminodifluoroborane, H_2NBF_2 , has been characterized as a volatile product of the pyrolysis of $\text{H}_3\text{N}, \text{BF}_3$ at 185 °C.^{13c} Polycyclic borazines (19) have been prepared from thioboranes.^{13d}

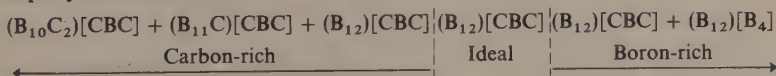


¹³ (a) E. Niecke and W. Bitter, *Angew. Chem. Internat. Edn.*, 1975, **14**, 56; (b) R. A. Kovar and G. G. Waldvogel, *Inorg. Chem.*, 1975, **14**, 2239; (c) E. F. Rothgery, H. A. McGee, jun., and S. Pusatcioglu, *Inorg. Chem.*, 1975, **14**, 2236; (d) R. H. Cragg and A. F. Weston, *J.C.S. Dalton*, 1975, 1961; (e) A. Serafini and J. F. Labarre, *J. Mol. Structure*, 1975, **26**, 129; (f) D. T. Haworth and V. M. Scherr, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2010; (g) A. DeStefano and R. F. Porter, *Inorg. Chem.*, 1975, **14**, 2882.

As regards σ - and π -components to bonding between boron and first-period elements, borazine $B_3N_3H_6$ and boroxine $B_3O_3H_3$ are key compounds. The influence of π -delocalization on the electronic structures of these planar six-membered ring compounds has been examined by *ab initio* SCF-LCAO-MO calculations.^{13e} In borazine there is a formal σ -charge transfer from H_B and B towards nitrogen (1.02e) and a much smaller π -charge transfer from N to B (0.35e). Thus nitrogen is more negatively charged. For boroxine, the σ -transfer from H_B and B to O is 1.14e and there is a reverse π -transfer of only 0.26e. Hence the direction of polarity of the B—O bond is similar to that of the B—N bond, the π -overlap population of the B—O bond is less, and the total charge transfer along the ring bonds is much larger in boroxine. In fluorinated boroxines the total ring population is decreased. Electron withdrawal through the σ -system is not counterbalanced by $F2p_\pi$ — $B2p_\pi$ bonding.^{13f} These calculations thus support the inferences made for these molecules on the basis of their chemical reactivities. In this context the likely structures (20) and (21) for the protonated borazine cation (*cf.* protonated benzene) have the proton located at a site close to nitrogen.^{13g}



Boron Carbides.—The history of the boron carbide crystal structure goes back 35 years to the initial description of a 15-atom unit cell containing a nearly regular icosahedron of boron atoms and a linear chain of supposedly three atoms linking icosahedra. Much later it was realized that the central atom of the three-atom chains was boron. This can be represented as $(B_{12})[CBC]$. The chemical composition B_4C can then be attained by the average substitution of \blacksquare carbon atom for boron in each icosahedron, *viz.* $(B_{11}C)[CBC]$, a feature which was very recently revealed by careful X-ray work. With the ideal, rhombohedral $(B_{12})[CBC]$ and carbon-rich $(B_{11}C)[CBC]$ structures established, the question remains as to structural modifications accompanying carbon depletion of the ideal $B_{13}C_2$ structure. The boron-carbon phase diagram indicates a single phase in the solubility range 9—20 atom % carbon. Several solutions to this problem have been suggested, none of which corresponds to the structure of a boron-rich boron carbide determined this year.¹⁴ The crystal system of this carbide (containing 8 ± 1 atom % C) is rhombohedral ($R\bar{3}m$) but unit cell parameters are significantly larger than for the material with 20% C. Icosahedra (B_{12}) are still present but one fourth of the linear $[CBC]$ chains in the $(B_{12})[CBC]$ structure are replaced by planar $[B_4]$ groups. Both terminal and bridge atoms of these $[B_4]$ units have five-fold co-ordination. Thus the following changes may accompany decreases in carbon content for boron carbide:



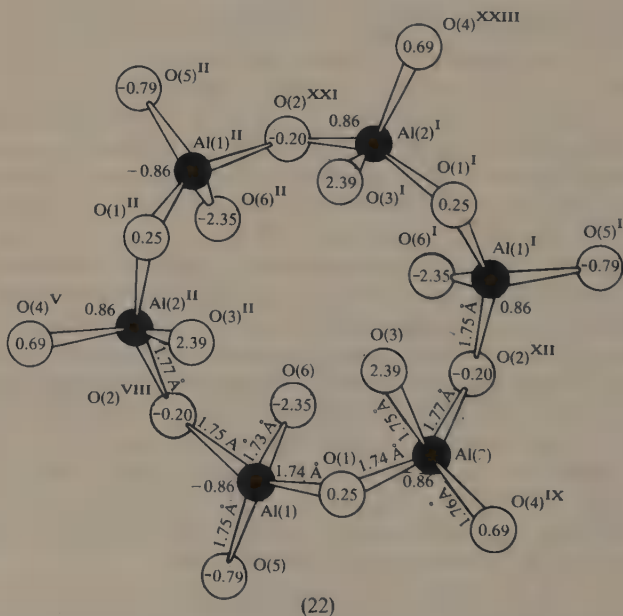
¹⁴ H. L. Yakel, *Acta Cryst.*, 1975, **B31**, 1695.

The extent to which the presence of increasing numbers of $[B_4]$ units in boron carbides contributes to the known solubility limits in the boron-carbon phase diagram remains to be deciphered.

2 Aluminium, Gallium, Indium, and Thallium

Structure and Bonding in Aluminates.—Two particular studies are singled out for mention. Few inorganic compounds are as essential to our society as tricalcium aluminate $3CaO, Al_2O_3$ (C_3A), a major component of Portland cement. Despite the efforts of numerous laboratories, dating back to 1929, the structure of C_3A remained unsolved until this year. The structure (22), finally elucidated by Mondal and Jeffrey^{15a} after 12 attempts, must stand as a monument in cement and aluminium-oxygen chemistry and consists of six AlO_4 tetrahedra (Al_6O_{18}), eight to a cell surrounding holes of radius 1.47 \AA , with Ca^{2+} ions in distorted six-fold co-ordination holding the rings together. The presence of rather short $Ca-O$ contacts (2.26 \AA) and the observed compression of CaO_6 octahedra may indicate that strain, together with the availability of large holes in the lattice, facilitates a rapid break-up of the structure on reaction with water to give the initial hydration product $2CaO, Al_2O_3, 8H_2O$ and finally the hexahydrate $3CaO, Al_2O_3, 6H_2O$. This structure should form the basis for an understanding of the effects of impurities on the reactivity of cement.

The SCF- X_α method has been used for the first time to calculate the electronic structure of the aluminate ion $[AlO_4]^{5-}$ for comparison with the isoelectronic and



¹⁵ (a) P. Mondal and J. W. Jeffrey, *Acta Cryst.*, 1975, **B31**, 689; (b) J. A. Tossell, *J. Amer. Chem. Soc.*, 1975, **97**, 4840.

isostructural $[\text{MgO}_4]^{6-}$ and $[\text{SiO}_4]^{4-}$ ions.^{15b} The calculated MO energies agree qualitatively with the separations of the $K_{\beta'}$ (assigned to the $3t_2$ MO) and K_{β} (assigned to the $4t_2$ MO) peaks in the X-ray emission spectrum. The calculations also indicated that peaks at 9.3 and 11.1 eV in the u.v. spectra of a natural phlogophite mica are due to the $[\text{AlO}_4]^{5-}$ unit. $\text{Si}3d\text{--O}2p$ (σ - and π -types) bonding does occur in the $[\text{SiO}_4]^{4-}$ ion but it is relatively small in magnitude compared with $\text{Si}3s\text{--O}2p$ and $\text{Si}3p\text{--O}2p$ bonding. For $[\text{AlO}_4]^{5-}$, the $5t_2$ MO is of similar energy to that in $[\text{SiO}_4]^{4-}$. Thus a small $\text{Al}3d\text{--O}2p$ bonding component may still be present. A sharp decrease in the strength of $\text{M}3s\text{--O}2p$ ($\text{M} = \text{Si}, \text{Al}, \text{or Mg}$) bonding is largely responsible for decreasing covalency and increasing instability of the tetrahedral clusters in the sequence $[\text{SiO}_4]^{4-} > [\text{AlO}_4]^{5-} > [\text{MgO}_4]^{6-}$.

The Co-ordination Sphere of Aluminium in Solution.—The n.m.r. probes ^1H , ^{27}Al , ^{31}P , and ^{13}C have all been utilized to investigate the inner co-ordination sphere of Al^{3+} . Solvation numbers of 6 are the rule. However, in ethanol $[\text{Al}(\text{EtOH})_4]^{3+}$ is the dominant species. By utilizing both ^{27}Al and ^{31}P n.m.r., Delpuech and co-workers¹⁶ have demonstrated the existence of octahedral $[\text{AlL}_6]^{3+}$ [$\text{L} = (\text{MeO})_3\text{PO}, (\text{EtO})_3\text{PO}, (\text{MeO})_2\text{MePO}, (\text{EtO})_2\text{EtPO}, \text{or } (\text{MeO})_2\text{HPO}$] and the tetrahedral solvate $[\text{AlL}_4]^{3+}$ [$\text{L} = (\text{Me}_2\text{N})_3\text{PO}$] in anhydrous nitromethane. Kinetic data are indicative of a dissociative $\text{S}_{\text{N}}1$ ligand-exchange mechanism for $[\text{AlL}_6]^{3+}$, while conversely an associative $\text{S}_{\text{N}}2$ mechanism is applicable to $[\text{Al}\{(\text{Me}_2\text{N})_3\text{PO}\}_4]^{3+}$. The activation energy for the associative process is dramatically smaller, by *ca.* 12 kcal mol⁻¹, and ligand exchange on Al^{3+} in $(\text{Me}_2\text{N})_3\text{PO}$ is five orders of magnitude faster than in systems where Al^{3+} is six-co-ordinate. These observations may have important implications for the synthetic and solution chemistry of Al^{3+} , especially if they can be generalized for other solvent systems. It is interesting that whereas activation enthalpies for exchange in $[\text{AlL}_6]^{3+}$ ($\text{L} = \text{DMF}$ or DMSO) seem to indicate dissociative pathways, for $[\text{GaL}_6]^{3+}$ ($\text{L} = \text{H}_2\text{O}$ or DMF) associative mechanisms may be operative. Halide ion exchange on $[\text{GaCl}_4]^-$ is also associative.

Aluminium-Halogen Compounds.—The heats of reaction of Group III halides and organometallics with neutral ligands containing Group V and VI donor atoms have been measured over the past 20 years in an attempt to compare acceptor properties. Recently Wood and co-workers^{17a} have determined the necessary heats of formation, crystal structures, and lattice energies for $\text{M}^1[\text{M}^2\text{X}_4]$ salts ($\text{M}^1 = \text{Na}$ or Cs , $\text{M}^2 = \text{Al}$ or Ga , $\text{X} = \text{Cl}$ or Br) to calculate $\text{M}^2\text{X}_3\text{--X}^-$ donor-acceptor bond energies. (Average heats of dissociation $D_{\text{M}^2\text{X}_3\text{--X}^-}$ (kcal mol⁻¹) are 82 ($[\text{GaCl}_4]^-$), 87 ($[\text{AlCl}_4]^-$), 75 ($[\text{GaBr}_4]^-$), and 80 ($[\text{AlBr}_4]^-$). Hence the halide ions form stronger donor-acceptor bonds than the neutral ligands. An estimate of the $\text{InCl}_3\text{--Cl}^-$ bond energy by a newly developed method suggests that towards the halide ions the order of acidities is $\text{InCl}_3 > \text{AlCl}_3 > \text{GaCl}_3$. These results can be compared with the relative acidity order $\text{BCl}_3 > \text{AlCl}_3 > \text{GaCl}_3 > \text{InCl}_3$ towards ethyl acetate as the reference base, the order $\text{Al} > \text{Ga} > \text{In}$ for Ph_3M^2 towards pyridine, and the common sequence

¹⁶ J. J. Delpuech, M. R. Khaddar, A. A. Peguy, and P. R. Rubini, *J. Amer. Chem. Soc.*, 1975, **97**, 3373.

¹⁷ (a) R. C. Gearhart, jun., J. D. Beck, and R. H. Wood, *Inorg. Chem.*, 1975, **14**, 2413; (b) G. K. Barker, M. F. Lappert, J. B. Pedley, G. J. Sharp, and N. P. C. Westwood, *J. C. S. Dalton*, 1975, 1765; (c) J. L. Dehmer, J. Berkowitz, L. C. Cusachs, and H. S. Aldrich, *J. Chem. Phys.*, 1974, **61**, 594; (d) K. Wittel and R. Manne, *J. Chem. Phys.*, 1975, **63**, 1322; (e) R. G. S. Pong, R. A. Stachnik, A. E. Shirk, and J. S. Shirk, *J. Chem. Phys.*, 1975, **63**, 1525.

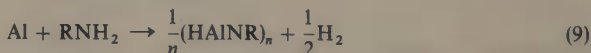
$\text{Al} > \text{B} \sim \text{Ga} > \text{In}$ for bulky amines. Additional information on $\text{M}-\text{X } p_{\pi}-p_{\pi}$ bonding and Lewis acidities for monomeric Group III acceptors has been sought using p.e. spectroscopy.^{17b} For gaseous MCl_3 ($\text{M} = \text{B}, \text{Al}, \text{Ga}, \text{or In}$), the relative orbital energies increase in sequence $a_2', e', e'', a_2'', e', a_1'$. The a_2'' orbital which is primarily responsible for π -bonding in MX_3 has energies indicative of greater $\text{M}-\text{X } \pi$ -bonding in the boron compounds. These authors suggest that the baricentre of the first two IP's for the MX_3 species provides an estimate of residual charge on the halogen atom and the relative π -density on the central metal atom. Thus $\text{Al} > \text{B} \sim \text{Ga} \gg \text{In}$, if this is considered a measure of Lewis acidity. However, the same criterion yields $\text{BCl}_3 \gg \text{BBr}_3$, contrary to the usual order of affinities. As a general observation, changes in electronic and structural properties for both donor and acceptor occur on complexation and reliable orders of acidities cannot generally be expected from a single physical measurement.

A further item of interest is the splitting observed in the e'' ionization energies of the iodides. Although Lappert *et al.* favoured a second-order spin-orbit interaction as an explanation of this effect, this has been rejected earlier.^{17c} Instead, it was proposed that GaI_3 had a pyramidal ground state. A reinterpretation of the phenomenon has since appeared, confirming the spin-orbit origin of the splitting.^{17d} Moreover, in argon matrices all of the gallium halide monomers are planar D_{3h} molecules, as intuitively expected.^{17e}

Compounds with Aluminium-Hydrogen Bonds.—One notable development in the past five years has been the synthesis and characterization of a series of poly-(*N*-alkyliminoalanes). Several routes to these compounds are available, *e.g.*



A simpler direct method has been developed:^{18a}



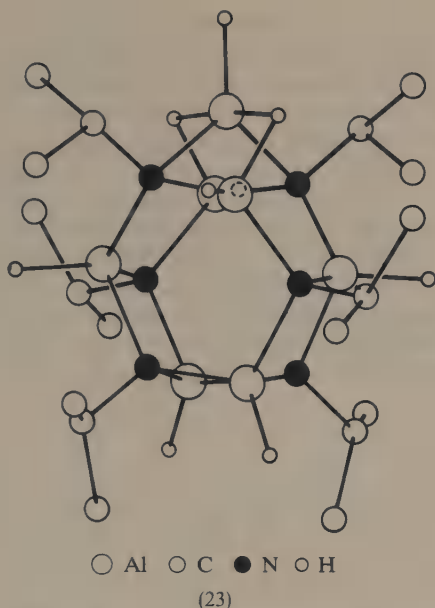
These polyiminoalanes have fascinating cage structures. A typical structure, that of the alane adduct $[\text{HAINPr}^i]_6\text{AlH}_3$ is shown in (23).^{18b}

Finally, mention should be made of an important study on the mechanism of hydroalumination of Group IV substituted alkynes.^{18c} For trimethyl(phenylethynyl)silane, a kinetically controlled *cis*-hydroalumination by R_2AlH is followed by a rapid isomerization to the *trans*-adduct. Carbon-silicon and/or carbon-aluminium $p_{\pi}-d_{\pi}$ bonding as in (24) and (25) may promote *cis-trans* isomerization.

Transition Metal-Gallium, -Indium, and -Thallium Bonds.—The chemistry of compounds with transition metal— M ($\text{M} = \text{Ga}, \text{In}, \text{or Tl}$) bonds has been developed. Reaction of Me_3Ga with $[\eta\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}]$ gave $[\eta\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_3\text{Ga}$.^{19a} The

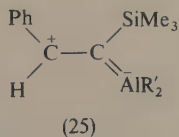
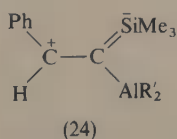
¹⁸ (a) S. Cucinella, A. Mazzei, and G. Dozzi, *J. Organometallic Chem.*, 1975, ■■, C19; (b) G. Perego, M. Cesari, G. Del Piero, A. Balducci, and E. Cernia, *J. Organometallic Chem.*, 1975, **87**, 33; (c) J. J. Eisch and S. G. Rhee, *J. Amer. Chem. Soc.*, 1975, **97**, 4673.

¹⁹ (a) A. J. Conway, P. B. Hitchcock, and J. D. Smith, *J.C.S. Dalton*, 1975, 1945; (b) A. T. T. Hsieh, *Inorg. Chim. Acta*, 1975, **14**, 87; (c) H. J. Haupt, F. Neumann, and H. Preut, *J. Organometallic Chem.*, 1975, **99**, 439; (d) S. G. Pedersen and W. R. Robinson, *Inorg. Chem.*, 1975, **14**, 2360; (e) S. G. Pedersen and W. R. Robinson, *Inorg. Chem.*, 1975, **14**, 2365.



stereochemistry of gallium is, as expected, trigonal planar. This complex completes the series $[\eta\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_3\text{M}$ ($\text{M} = \text{Ga}, \text{In}, \text{or Tl}$).^{19b} Interestingly, the corresponding aluminium complex $[\eta\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]\text{Al}\cdot 3\text{THF}$ does *not* contain Al—W bonds. Treatment of indium metal with $[\text{Re}_2(\text{CO})_{10}]$ in a bomb afforded $[\text{Re}_2(\text{CO})_8\{\mu\text{-InRe}(\text{CO})_5\}_2]$ (*cf.* $[\text{Mn}_2(\text{CO})_8\{\mu\text{-InMn}(\text{CO})_5\}_2]$) and $[\text{Re}_4(\text{CO})_{12}\{\mu^3\text{-InRe}(\text{CO})_5\}_4]$ having a tetracapped tetrahedral structure.^{19c} There is an obvious analogy between the terminal transition-metal moieties in these species and bulky alkyl groups. Furthermore, the instability usually associated with Tl^{I} organometallics is apparent in the behaviour of Tl^{I} —transition metal bonds.^{19d,e} Thus, reaction of $\text{Tl}[\text{Co}(\text{CO})_4]$ with a phosphine (L) causes disproportionation to thallium metal and $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$. Only less basic phosphites yield Tl^{I} derivatives. Thallium(I)—iron, —vanadium, or —chromium bonds are only stable when the corresponding transition-metal anion is weakly basic.^{19e}

Synthesis of Indium (III) and Indium (I) Compounds.—The development of a direct electrochemical synthesis of indium compounds warrants special mention.^{20a} The method, which can be used to produce neutral, anionic, or cationic complexes, uses a cell with an indium anode, a platinum cathode, and a non-aqueous solvent system



²⁰ (a) J. J. Habeeb and D. G. Tuck, *J.C.S. Chem. Comm.*, 1975, 808; (b) J. J. Habeeb and D. G. Tuck, *J.C.S. Dalton*, 1975, 1815.

(usually benzene-methanol). Applied voltages of 50–100 V at 20–100 mA for 1–3 h gave gram quantities of complexes. The facile synthesis of anhydrous InCl_3 (cf. burning indium metal in an atmosphere of dry chlorine gas) and $\text{Et}_4\text{N}[\text{InI}_2]$ (from Et_4NI , I_2 , and In) are notable. Apparently the method can be extended to the synthesis of transition-metal halide compounds, e.g. CrCl_3 and may therefore be applicable to organometallics. Developments will be awaited with interest.

The co-ordination chemistry of indium(I) has been slow to develop, owing principally to the intractability of potential precursors such as InCl , In_2O , and In_2S . This is in marked contrast to the isoelectronic tin(II) species such as SnCl_2 which have been extensively investigated both as Lewis acids and as useful synthetic reagents. Structural data for indium(I) compounds are very sparse when compared to those available for tin(II). Habeeb and Tuck^{20b} have used cyclopentadienylin-dium(I) as an organic solvent-soluble starting material. The reaction



yielded various indium(I) complexes, including 4,4,4-trifluoro-1-(thien-2-yl)butane-1,3-dionatoindium(I), quinolin-8-olatoindium(I), and 2-mercap-topentan-3-onatoindium(I). These indium(I) compounds, e.g. quinoline-8-olatoindium(I) $[\text{In}(\text{qno})]$, may in their own right be useful starting materials for indium(III) complexes. Thus, acetylacetone yielded $[\text{In}^{\text{III}}(\text{qno})(\text{acac})_2]$ and iodine $[\text{In}(\text{qno})\text{I}_2]$. The availability of soluble In^{I} compounds such as $[\text{In}(\text{qno})]$ may be of considerable use in extending the range of compounds having indium-transition metal bonds *via* oxidative addition reactions (see above).

Pentahalogenometallates(III).—New vibrational data for single crystals of the square-pyramidal ions $[\text{MCl}_5]^{2-}$ ($\text{M} = \text{In}$ or Tl) together with low-temperature Raman and i.r. studies of polycrystalline samples allow a reassignment of vibrational spectra.²¹ In the isomorphous tetraethylammonium salts, $[\text{MCl}_5]^{2-}$ ions reside on sites of C_2 symmetry rather than C_4 as assumed in previous analyses based on X -ray data. Rerefinement of the earlier X -ray data in the space group $P4$, including anisotropic temperature factors, gave an improved R value of 0.067. However, the basic structural features of the molecules remain unchanged.

Stereochemical Activity of the Thallium(I) Lone Pair.—Although the ions Ga^+ , In^+ , and Tl^+ have ns^2 configurations there has been little structural evidence to indicate whether this pair of electrons is 'inert' or stereochemically active. X -ray studies of hexafluoroacetylacetonatothallium(I),^{22a} $(\text{Bu}^i_2\text{NCS}_2)\text{Tl}$,^{22b} and Tl_2S_5 ^{22c} have now shown unequivocally that the $6s^2$ pair plays a major role in dictating the co-ordination geometry around the thallium atom.

²¹ G. Joy, A. P. Gaughan, jun., I. Wharf, D. F. Shriver, and J. P. Dougherty, *Inorg. Chem.*, 1975, **14**, 1795.

²² (a) S. Tachiyashiki, H. Nakayama, R. Kuroda, S. Sato, and Y. Saito, *Acta Cryst.*, 1975, **B31**, 1483; (b) H. Pritzkow and P. Jennische, *Acta Chem. Scand.*, 1975, **A29**, 60; (c) B. Leclerc and T. S. Kabre, *Acta Cryst.*, 1975, **B31**, 1695.

PART III: Groups IV and V

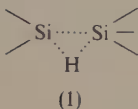
By J. D. Smith

1 Reactions of Hydrides

The pyrolysis of silanes is proving as complicated and difficult to sort out as the pyrolysis of hydrocarbons, but interest in the subject is maintained by the differences between the chemistry of carbon and that of the other Group IV elements. For example, the initial step in the thermal decomposition of hydrocarbons is the breaking of a C—H or C—C bond, with formation of radical intermediates $R_3C\cdot$. However, it has been shown, *e.g.* by deuterium substitution studies, that the initial step in the decomposition of polysilanes results in elimination of silenes $:SiH_2$ or $:SiHR$.^{1a}



Activation energies for this process (*ca.* 210 kJ mol⁻¹) are less than Si—Si bond energies (*ca.* 340 kJ mol⁻¹) and it seems that the reaction must involve a 1,2-hydrogen shift with a transition state (1):



A similar transition state for hydrocarbon decompositions would involve quinquivalent carbon and this is apparently energetically unfavourable. The detailed mechanism of the decomposition of monosilane SiH_4 is still not clear, but evidence from pyrolysis in the presence of acetylene^{1b} shows that silyl radicals $\cdot SiH_3$, rather than silene species $:SiH_2$, are the predominant intermediates produced in the first step. It has been suggested that formation of ground-state singlet $:SiH_2$ from SiH_4 is forbidden by orbital symmetry unless the reaction path is such as to add considerable strain energy to the activation energy; $\cdot SiH_3$ formation is thus favoured. Ground-state $:SiH_2$ could be generated by an orbitally allowed process from disilane, and ethynylsilane, $HC\equiv CSiH_3$, from $:SiH_2 + HC\equiv CH$, is indeed found as a major product in the pyrolysis of disilane-acetylene mixtures.

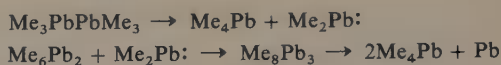
After further studies on the pyrolysis of hexamethyldisilane, a mechanism has been proposed^{1c} which accounts for some of the divergent results, obtained under a variety of conditions, in earlier work. Initial steps in the decomposition give trimethylsilyl radicals $Me_3Si\cdot$ or dimethylsilene $Me_2Si:$, both of which react further to give a complicated mixture.



A new value of 337 kJ mol⁻¹ for the bond dissociation energy $D(Me_3Si-SiMe_3)$ has been deduced. The thermal decomposition of hexamethyldilead in toluene can be

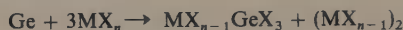
¹ (a) A. J. Vanderwielen, M. A. Ring, and H. E. O'Neal, *J. Amer. Chem. Soc.*, 1975, **97**, 993; (b) C. H. Haas and M. A. Ring, *Inorg. Chem.*, 1975, **14**, 2253; (c) I. M. T. Davidson and A. V. Howard, *J.C.S. Faraday I*, 1975, **71**, 69 and references therein; (d) D. P. Arnold and P. R. Wells, *J.C.S. Chem. Comm.*, 1975, 642.

explained in terms of the following reaction sequence:



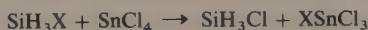
In this case, no evidence for methyl or trimethyl-lead radicals $\text{Me}_3\text{Pb}\cdot$ was obtained.^{1d}

Information about reactive species may also be obtained from reactions of metal atoms, obtained by evaporation at high temperatures ($>1000^\circ\text{C}$) and in high vacuum (<1 Torr). The atoms and molecules of volatile compounds are brought together at a cold surface on which products are condensed (see also p. 179).^{2a} Particular attention has been given to the chemistry of carbon, silicon, and transition-metal atoms, but the first reports^{2b,c} of reactions of thermally generated germanium atoms have now appeared. The halides of carbon and silicon react with germanium atoms to give trihalogenogermyl derivatives and trimethylsilane reacts to give the new compound $\text{Me}_3\text{SiGeH}_2\text{SiMe}_3$:



There is interest in whether the initially produced atoms are in the ground (3P) or excited (1S or 1D) states and whether the electrons in intermediates such as HGeSiMe_3 or ClGeCCl_3 remain unpaired or relax to a paired configuration before further reaction.

Silyl compounds react with tin tetrachloride in two distinct ways.^{3a} With SiH_4 , SiH_3F , SiH_3Cl , $(\text{SiH}_3)_3\text{N}$, $[\text{SiH}_3\text{Mn}(\text{CO})_5]$, or Si_2H_6 , chlorine is substituted for hydrogen and SiH_2Cl derivatives are isolated. With SiH_3Br , $[\text{SiH}_3\text{Co}(\text{CO})_4]$, $(\text{SiH}_3)_2\text{S}$, or $(\text{SiH}_3)_3\text{P}$, the predominant reaction is exchange:



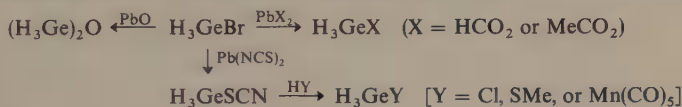
The compounds XSnCl_3 sometimes undergo further reactions. With $(\text{SiH}_3)_2\text{O}$ there is evidence for both substitution and exchange. In general, the exchange reaction occurs when the silyl starting materials SiH_3X have heavier, less electronegative groups X.

The germyl derivatives H_3GeM ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$) have been made from germane and the alkali metal in dimethoxyethane, and the potassium, rubidium, and caesium compounds have been isolated as crystalline solids.^{3b} Solvent-free H_3GeLi and H_3GeNa could not be obtained. A single-crystal X-ray investigation has shown that germyl-potassium and -rubidium, like silyl-potassium, -rubidium, and -caesium, have the sodium chloride structure, in which germyl anions show free rotation at room temperature. Germylcaesium has the rare thallium iodide structure in which

² (a) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 121; (b) M. J. McGlinchey and T.-S. Tan, *Inorg. Chem.*, 1975, **14**, 1209; (c) R. T. Conlin, S. H. Lockhart, and P. P. Gaspar, *J.C.S. Chem. Comm.*, 1975, 825.

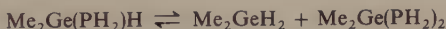
³ (a) S. Craddock, E. A. V. Ebsworth, and N. Hosmane, *J.C.S. Dalton*, 1975, 1624; (b) G. Thirase, E. Weiss, H. J. Hennig, and H. Lechert, *Z. anorg. Chem.*, 1975, **417**, 221; (c) P. C. Angus and S. R. Stobart, *J.C.S. Dalton*, 1975, 2342; (d) A. R. Dahl, C. A. Heil, and A. D. Norman, *Inorg. Chem.*, 1975, **14**, 1095. (e) A. R. Dahl, A. D. Norman, H. Shenav, and R. Schaeffer, *J. Amer. Chem. Soc.*, 1975, **97**, 6364; (f) A. R. Dahl and A. D. Norman, *Inorg. Chem.*, 1975, **14**, 1093; (g) A. R. Dahl, C. A. Heil, and A. D. Norman, *Inorg. Chem.*, 1975, **14**, 2562; (h) J. E. Drake and C. Riddle, *J. Chem. Soc. (A)*, 1968, 2709; *Quart. Rev.*, 1970, **24**, 263.

each germyl ion has seven caesium neighbours and each caesium seven germyl neighbours. At low temperatures (below -100°C for H_3GeK , -120°C for H_3GeRb , and -170°C for H_3GeCs) rotation of the germyl anion is frozen, as shown by broad-line n.m.r. experiments. The GeH_3^- ionic radius (assuming values of K^+ , 1.33 \AA ; Rb^+ , 1.48 \AA) is 2.29 \AA , only a little larger than that of the H_3Si^- ion (2.26 \AA). Bond angles (from broad-line n.m.r.) are for SiH_3^- $94 \pm 4^\circ$ (*cf.*, PH_3 , 94°) and for GeH_3^- $93 \pm 4^\circ$ (*cf.*, AsH_3 , 92°). The conversion of bromogermane into a variety of germyl derivatives by use of lead salts has been explored.^{3c} In general, the conversions are cleaner and the yields are higher than with the more reactive silver salts. Good yields of germyl formate and acetate have been obtained and digermyl ether has been made from bromogermane and lead oxide. Reactions with lead cyanate or thiocyanate gave germyl isocyanate or isothiocyanate (Scheme 1). Germyl trifluoroacetate was made from bromogermane and silver trifluoroacetate.

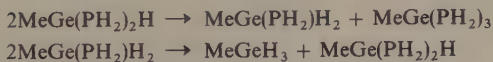


Scheme 1

The chemistry of phosphinogermanes $\text{R}_n\text{Ge}(\text{PH}_2)_{4-n}$ ($\text{R} = \text{alkyl or H}$), made from the chlorogermanes and $\text{LiAl}(\text{PH}_2)_4$ in glyme solvents, has been investigated in some detail.^{3d-g} For example, redistribution reactions have been studied by n.m.r. spectroscopy.^{3d} The products from dimethyl(phosphino)germane, $\text{Me}_2\text{Ge}(\text{PH}_2)_2\text{H}$, at equilibrium showed roughly statistical distribution of phosphino- and hydrido-substituents at germanium:

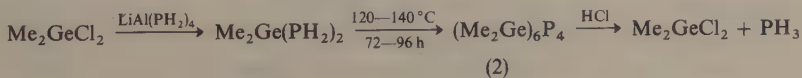


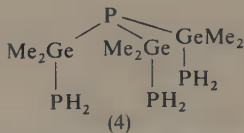
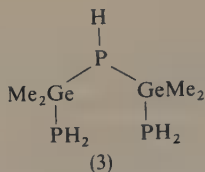
Redistribution reactions of methyldiphosphinogermane were also clearly detected:



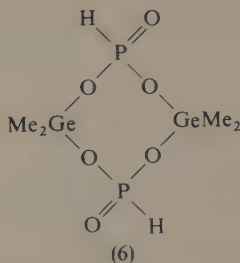
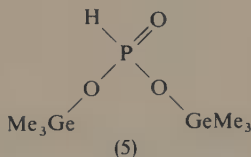
From phosphinogermane, H_3GePH_2 , the products indicated redistributions both at germanium and, more slowly, at phosphorus. New ternary hydrides $\text{H}_2\text{Ge}(\text{PH}_2)_2$ and $\text{HGe}(\text{PH}_2)_3$, as well as GeH_4 , were formed rapidly, and the products $(\text{H}_3\text{Ge})_2\text{PH}$, $(\text{H}_3\text{Ge})_3\text{P}$, and PH_3 after long reaction times.

Pyrolysis of the more thermally stable dialkyldiphosphinogermanes $\text{R}_2\text{Ge}(\text{PH}_2)_2$ ($\text{R} = \text{Me or Et}$) resulted in elimination of phosphine and formation of the cage compound hexa(dialkylgerma)tetraphosphide (2), characterized by spectral data, by reaction with hydrogen chloride (which confirms the presence of $\text{Ge}-\text{P}$ and the absence of $\text{Ge}-\text{Ge}$ and $\text{P}-\text{P}$ bonds), and by an X-ray study^{3e} (see next section). The $\text{Ge}-\text{P}$ distance is 2.317 \AA . By careful separation of products two intermediates (3) and (4) were characterized, but the detailed mechanism of the condensation process was not completely established.





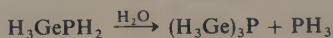
Since oxidation products appeared to be catalysts in the formation of the cage compound (2), the reactions between trimethyl(phosphino)germane, Me_3GePH_2 , or dimethylbis(phosphino)germane, $\text{Me}_2\text{Ge}(\text{PH}_2)_2$, and oxygen in chloroform solution were studied in more detail. The products were intractable solids, phosphines or phosphine oxidation products, but traces of new germyl phosphonates, (5) and (6), were obtained. One of these (6) has been made in 70% yield from the dimethylgermanium oxides $(\text{Me}_2\text{GeO})_n$ and a ten-fold excess of anhydrous phosphorous acid.^{3f}



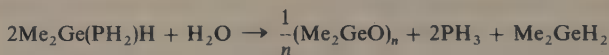
Hydrolysis^{3g} of the methyl(phosphino)germanes Me_3GePH_2 and $\text{Me}_2\text{Ge}(\text{PH}_2)_2$ appears to be quantitative, *e.g.*



No evidence has been obtained for redistribution reactions at phosphorus, such as those observed earlier for unsubstituted germylphosphine:^{3h}



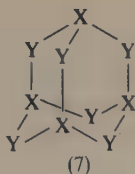
Hydrolysis of dimethyl(phosphino)germane, $\text{Me}_2\text{Ge}(\text{PH}_2)_2$, was more complex, as the $\text{Ge}-\text{H}$ bond was labile under the reaction conditions. With short reaction times (20–100 min) and a deficiency of water, the compound $(\text{Me}_2\text{GeH})_2\text{O}$ was formed, but this was thermally unstable at 32 °C and readily converted by water into $(\text{Me}_2\text{GeO})_n$. With reaction times greater than 2 h, the hydrolysis could be described by the following equation:



No Me_2GeH_2 was detected until after $(\text{Me}_2\text{GeH})_2\text{O}$ had begun to disappear.^{3g}

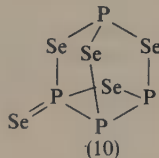
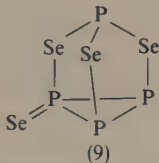
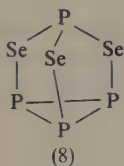
2 Cage Compounds

A large number of molecules X_4Y_6 (7), where $\text{X} = \text{RE}^1$ or E^2 , $\text{Y} = \text{R}_2\text{E}^1$, RE^2 , or E^3 , and E^1 , E^2 , and E^3 are elements from Groups IV, V, and VI respectively, are known. Most of these have the adamantane structure with symmetry T_d or close to T_d .



Full details of the crystal structure of $(\text{MeSi})_4\text{S}_6$ have been published;^{4a} the molecule is of a well established series and the germanium and tin analogues are isostructural. Hexa(dimethylgermana)tetraphosphide (2) has a similar structure (7; $\text{X} = \text{P}$, $\text{Y} = \text{Me}_2\text{Ge}$).^{3e} The phosphorus atom of the cage compound P_4O_6 (7; $\text{X} = \text{P}$, $\text{Y} = \text{O}$) is a donor towards some transition metals. Under a carbon monoxide atmosphere, the carbonyl $[\text{Fe}_2(\text{CO})_9]$ reacted with the oxide P_4O_6 in THF to give a series of compounds $[\{(\text{CO})_4\text{Fe}\}_n(\text{P}_4\text{O}_6)]$ ($n = 1-4$) which was characterized by n.m.r. spectroscopy.^{4b} Reactions with pentacarbonyl iron were more complicated and the products included the oxides P_4O_7 and P_4O_9 .

Another new cage compound synthesized during 1975 is the selenide P_4Se_4 , made by fusing together the elements at $300-350^\circ\text{C}$.^{4c} Its i.r. spectrum was consistent with the structure (9) similar to those of the known selenides P_4Se_3 (8) and P_4Se_5 (10).^{4d}



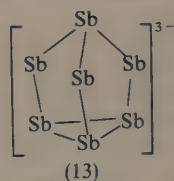
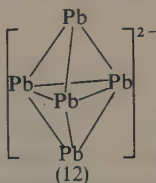
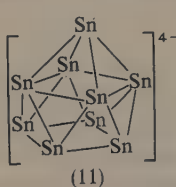
3 Polyatomic Anions

Alloys of the post-transition metals Sn, Pb, Sb, or Bi with alkali metals are remarkably soluble in liquid ammonia, and a series of potentiometric and preparative studies more than 40 years ago^{5a} suggested that the coloured solutions contained the cluster anions Sn_9^{4-} , $\text{Pb}_{7,9}^{4-}$, $\text{Sb}_{3,5,7}^{3-}$, and $\text{Bi}_{3,5}^{3-}$. Confirmation of these clusters by X-ray crystallography has so far proved impossible, because, on evaporation of the ammonia, the Na^+ and M_n^{m-} ions revert to the metallic alloys. The isolation last year^{5b} of the crystalline compound $\text{Na}(\text{crypt})^+\text{Na}^-$ [$\text{crypt} = \text{N}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_3\text{N}$] has suggested a new approach to a long-standing problem. Small alloy samples have been treated with the crown ether in ethylenediamine. Crystalline compounds $[\text{Na}(\text{crypt})^+]_m\text{M}_n^{m-}$ have been obtained

⁴ (a) J. C. J. Bart and J. J. Daly, *J.C.S. Dalton*, 1975, 2063; (b) M. L. Walker and J. L. Mills, *Inorg. Chem.*, 1975, **14**, 2438; (c) Y. Monteil and H. Vincent, *Z. anorg. Chem.*, 1975, **416**, 181; (d) G. J. Penney and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1971, 245; E. Keulen and A. Vos, *Acta Cryst.*, 1959, **12**, 323.

⁵ (a) E. Zintl, J. Goubeau, and W. Dullenkopf, *Z. phys. Chem.*, 1931, **154A**, 1; (b) F. J. Tehan, B. L. Barnett, and J. L. Dye, *J. Amer. Chem. Soc.*, 1974, **96**, 7203; (c) J. D. Corbett and P. A. Edwards, *J.C.S. Chem. Comm.*, 1975, 984; (d) A. Hershaft and J. D. Corbett, *Inorg. Chem.*, 1963, **2**, 979; (e) R. M. Friedman and J. D. Corbett, *Inorg. Chem.*, 1973, **12**, 1134; (f) J. D. Corbett, *Inorg. Chem.*, 1968, **7**, 198; (g) J. D. Corbett, D. G. Adolphson, D. J. Merryman, P. A. Edwards, and F. J. Armatas, *J. Amer. Chem. Soc.*, 1975, **97**, 6267; (h) W. Dahlmann and H. G. von Schnering, *Naturwiss.*, 1972, **59**, 420; *ibid.*, 1973, **60**, 429; (i) U. Frank and W. Müller, *Z. Naturforsch.*, 1975, **30b**, 313.

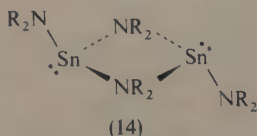
and the structures of three anions, Sn_9^{4-} , Pb_5^{2-} , and Sb_7^{3-} have been determined. Although the anion Sn_9^{4-} has the same valence electron structure^{5c} as the trigonal-bipyramidal (D_{3h}) Bi_9^{5+} isolated in 'bismuth monochloride', $[(\text{Bi}_9^{5+})_2(\text{BiCl}_5^{2-})_4(\text{Bi}_2\text{Cl}_8^{2-})]$,^{5d} and in $[\text{Bi}^+(\text{Bi}_9^{5+})(\text{HfCl}_6^{2-})_3]$,^{5e} the structure (11) is an antiprism capped on one square face (C_{4v}) ($\text{Sn}-\text{Sn} = 2.93\text{--}3.31 \text{ \AA}$).



That such a configuration is obtainable in a crystalline compound is consistent with the molecular orbital scheme proposed earlier.^{5f} The green Pb_9^{4-} , established in liquid ammonia and isoelectronic with Bi_9^{5+} , has not yet been obtained in a crystalline derivative, but Pb_5^{2-} , also with D_{3h} symmetry (12) and $\text{Pb}-\text{Pb} \text{ 3.00--3.23 \AA}$, has been obtained.^{5c} This ion is isoelectronic with the well established Bi_5^{3+} ion. The Sb_7^{3-} ion, found^{5g} in $[\text{Na}(\text{crypt})^+]_3\text{Sb}_7^{3-}$ has approximate C_{3v} symmetry (13) ($\text{Sb}-\text{Sb} \text{ 2.69--2.88 \AA}$); the cluster is similar to the P_7^{3-} cluster in Sr_3P_{14} and Ba_3P_{14} ^{5h} and the valence structure is presumably the same as in the well-established compounds P_4S_3 , P_4Se_3 , and As_4S_3 [*cf.* structures (13) and (8)]. Planar five-membered rings Ge_5 have been characterized⁵ⁱ in the new lithium germanide $\text{Li}_{11}\text{Ge}_6$, made by fusing the elements in a tantalum vessel, but there are no metal clusters in $\text{Li}_{13}\text{Sn}_5$ and a number of other solid phases in the lithium-tin and lithium-lead systems.

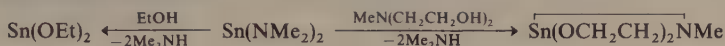
4 Alkylamido-derivatives and Alkoxides

The chemistry of dialkylamido-compounds of tin(IV) has been extensively studied but simple dialkylamido-derivatives $\text{Sn}(\text{NR}_2)_2$ are rare. Most of those reported contain large R groups, *e.g.* $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ or $\text{Sn}[\text{N}(\text{SiMe}_3)\text{Bu}^t]_2$.^{6a} It has now been found,^{6b} however, that bis(dimethylamido)tin(II) is accessible from the reaction between tin(II) chloride and LiNMe_2 . It is a white crystalline solid, m.p. $91\text{--}93^\circ\text{C}$, subliming at 70°C under 10^{-4} Torr and very reactive towards air and moisture. Only peaks from fragmentation of monomer are observed in the mass spectrum, but bis(dimethylamido)tin(II) appears to be dimeric in cyclohexane. The n.m.r. spectrum at 40°C shows only one line, but at -40°C there are two equal intense signals and at least three weaker peaks. The spectrum suggests that the dominant species is the *trans*-isomer (14), which has two non-equivalent sets of methyl groups. There may



⁶ (a) D. H. Harris and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 895; (b) P. Foley and M. Zeldin, *Inorg. Chem.*, 1975, **14**, 2264; (c) R. Gsell and M. Zeldin, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1133; (d) P. F. R. Ewings and P. G. Harrison, *J.C.S. Dalton*, 1975, 2015.

be smaller concentrations of the *cis*-isomer also. At 40 °C, exchange of alkylamido-groups between isomers and between bridge and terminal positions must be rapid on the n.m.r. time-scale to account for the single peak. The reactions of bis(dimethylamido)tin(II) appear to be similar to those of the tin(IV) compounds. For example, dimethylamine is rapidly eliminated in reactions with ethanol or *N*-methyldiethanolamine:



Spectroscopic properties of tin(II) alkoxides and phenoxides Sn(OR)_2 ($\text{R} = \text{alkyl}$ or aryl) have been reported; some of these compounds may be sublimed but most are insoluble in organic solvents and are thought to have polymeric solid-state structures. Sn(Obu)_2 , made by the well established procedure from tin(II) chloride, butanol, and triethylamine, is dimeric in dichloromethane.^{6c} Phenoxides may be made in quantitative yield from bis(methylcyclopentadienyl)tin and phenols.^{6d}

5 Lone-pair Stereochemistry

The valence-shell electron-pair repulsion (VSEPR) theory provides one of the simplest interpretations of the shapes of many compounds of the main-group elements. It is usually illustrated by use of compounds with electronegative atoms such as oxygen, fluorine, or nitrogen and it successfully predicts the unsymmetrical environments in compounds of elements with lone pairs such as Sn^{II} , Pb^{II} , Sb^{III} , or Bi^{III} . In solid compounds with the heavier non-metals, however, post-transition metals in low oxidation states often have symmetrical environments, in which lone pairs do not appear to occupy co-ordination positions. The compound $\text{CsSn}^{\text{II}}\text{Br}_3$ has now been shown^{7a} by a single-crystal *X*-ray study to have the ideal perovskite structure at room temperature, so each tin atom is surrounded by six bromine atoms at the corners of an octahedron, as suggested earlier from ^{119}Sn Mössbauer data. The compound is a black semiconductor and thus differs from the white compounds MSnBr_3 ($\text{M} = \text{Na, K, Rb, or NH}_4$). It is suggested that the colour, the electrical properties, the low Mössbauer chemical shifts, and the symmetrical environment of the tin(II) can all be accounted for by postulating that the $5s^2$ electrons are delocalized into a band formed by the bromine orbitals. Low-temperature Mössbauer data indicate that the tin(II) environment becomes less symmetrical at low temperatures. Coloured, high-temperature phases of other caesium bromostannates(II) *e.g.* $\text{CsSn}^{\text{II}}_2\text{Br}_5$ or $\text{Cs}_4\text{Sn}^{\text{II}}\text{Br}_6$, may also be obtained, and their properties are accounted for in the same way. At 20 °C the colours fade and the crystal symmetry becomes non-cubic; it is suggested that this indicates depopulation of the conduction band. The white compound $\text{Cs}_2\text{Sn}^{\text{IV}}\text{Br}_6$ has a cubic structure closely related to that of $\text{CsSn}^{\text{II}}\text{Br}_3$, and a series of solid solutions $\text{Cs}_2\text{Sn}^{\text{IV}}\text{Br}_6\text{--CsSn}^{\text{II}}\text{Br}_3$ may be obtained. The intense colours of these substances, which contain both Sn^{IV} and Sn^{II} , may also result from delocalization of the Sn^{II} lone pair into a conduction band formed by the bromine atoms. Electronic structures of mixed-valence compounds of antimony^{7b} and hexahalogenotellurates(IV)^{7c} may be discussed in similar terms.

⁷ (a) J. D. Donaldson, J. Silver, S. Hadjiminolis, and S. D. Ross, *J.C.S. Dalton*, 1975, 1500; (b) L. Atkinson and P. Day, *J. Chem. Soc. (A)*, 1969, 2423, 2432; (c) J. D. Donaldson, S. D. Ross, J. Silver, and P. J. Watkiss, *J.C.S. Dalton*, 1975, 1980.

6 Trends in Bond Order

The value of structural information is considerably enhanced where data are available for a closely related series of molecules. This point is illustrated by two examples.

Reactions between the lithium salt of diphenylketimine and the appropriate Group IV tetrachlorides yield the derivatives $E(NCPh_2)_4$ ($E = Si, Ge, \text{ or } Sn$):



Surprisingly, these compounds are not isomorphous, and there is a systematic variation in the $E-N$ distances and $E-N=C$ angles in the series (Table 1).^{8a}

Table 1 $E-N$ Bond lengths and $E-N=C$ angles in the compounds $E(NCPh_2)_4$

| E | Mean $E-N/\text{\AA}$ | Mean $E-N=C/^\circ$ | $E-N/\text{\AA}$ (calc.) | Difference/ \AA |
|----|--------------------------|------------------------|--------------------------|--------------------------|
| Si | 1.717(10) | 137.0 | 1.879 | 0.162 |
| Ge | 1.872(5) | 127.0 | 1.928 | 0.056 |
| Sn | 2.06(4) | 121.3 | 2.108 | 0.048 |

Each molecule has a tetrahedral arrangement of nitrogen atoms about the Group IV element. The structural differences between the silicon and germanium compounds cannot be attributed simply to differences in size, as the radii of silicon and germanium are quite similar. A possible explanation is that in the series from tin to silicon the hybridization at nitrogen changes from sp^2 to sp , as the lone pair is transferred to a p -orbital, which can more effectively interact with silicon through $(p-d)\pi$ bonds. Single-bond lengths may be estimated (Table 1) by combining well established $E-C$, $C-C$, and $C-N$ bond lengths, and there is a systematic shortening, decreasing in the series $Si > Ge > Sn$, in accord with the π -bonding hypothesis. The $(p-d)\pi$ overlap may be achieved by a variety of combinations of the four $E-N$ orbitals, and it is noticeable that the $E-N=C$ bond angles are extremely variable, especially in the silicon and germanium compounds. The choice of angles in a given crystal thus seems to depend on packing considerations – which explains the variety of molecular conformations found. In the silicon compound there are two crystallographically independent molecules with a range of $E-N=C$ angles.

Another example of a systematic study designed to detect trends in molecular parameters has involved the trimethyl-phosphine and -arsine oxides and sulphides.

Table 2 Molecular parameters for Me_3EY ($E = P \text{ or } As, Y = O \text{ or } S$)

| | Me_3PO | Me_3PS | Me_3AsO | Me_3AsS |
|---------------------|----------|----------|-----------|-----------|
| $E-Y/\text{\AA}$ | 1.476(2) | 1.940(2) | 1.631(3) | 2.059(3) |
| $E-C/\text{\AA}$ | 1.809(2) | 1.818(2) | 1.937(2) | 1.940(3) |
| $\angle YEC/^\circ$ | 114.4(7) | 114.1(2) | 112.6(3) | 113.4(4) |

Electron diffraction measurements (Table 2)^{8b} show that the $E-C$ distances decrease very slightly but systematically in the series X_3E , X_3ES , and X_3EO

^a (a) N. W. Alcock, M. Pierce-Butler, G. R. Willey, and K. Wade, *J.C.S. Chem. Comm.*, 1975, 183; N. W. Alcock and M. Pierce-Butler, *J.C.S. Dalton*, 1975, 2469; (b) G. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen, and K. Hedberg, *J. Amer. Chem. Soc.*, 1975, **97**, 6352.

(X = Me), as has been found for X = F or Cl. There is also a systematic decrease in P—O and P—S distances in the series Me₃PY, Cl₃PY, and F₃PY. Trends are attributed to changes in bond polarity. By making reasonable assumptions about the lengths of E—Y single bonds, it is found that P=S and As=S bonds have orders close to two, but P=O and As=O bonds appear to have higher orders. The rotational freedom of the methyl group increases in the series Me₃PO < Me₃PS ~ Me₃AsO < Me₃AsS.

7 Gas-phase Basicities

One of the major problems in the interpretation of results of preparative experiments in terms of molecular properties is in the allowance which should be made for solvation effects. The availability in recent years of measurements made on molecules in the gas phase, e.g. by ion cyclotron resonance spectroscopy,^{9a} has enabled much progress to be made. The gas-phase basicity of trimethylarsine has now been measured and this may be placed in the context of various amines and phosphines (Table 3).^{9b}

Table 3 Proton affinities *A*, ionization potentials *I*, and bond dissociation energies *D*(B⁺—H) (all in kJ mol⁻¹)

| Base B | <i>A</i> | <i>I</i> | <i>D</i> (B ⁺ —H) |
|--------------------|----------|----------|------------------------------|
| NH ₃ | 841 | 983 | 512 |
| MeNH ₂ | 878 | 865 | 431 |
| Me ₂ NH | 904 | 795 | 387 |
| Me ₃ N | 921 | 754 | 364 |
| PH ₃ | 783 | 961 | 432 |
| MePH ₂ | 841 | 879 | 408 |
| Me ₂ PH | 889 | 817 | 394 |
| Me ₃ P | 926 | 773 | 387 |
| AsH ₃ | 756 | 954 | 397 |
| Me ₃ As | 876 | 761 | 326 |

For all three groups of compounds, amines, phosphines, and arsines, the gas-phase basicities increase as hydrogen atoms are replaced by methyl groups. The effect is greater in phosphines and arsines than in amines in which, it is suggested, rehybridization energy in going from unprotonated to protonated amine opposes the effect of methyl substitution. Ion-molecule reactions of trimethylarsine are very like those of trimethylphosphine.

Another approach which leads to detailed information about bonding in simple molecules is exemplified by studies^{9c} on the phosphines R_nPX_{3-n} (R = Me or Bu^t; X = H, Cl, or F; *n* = 1—3) and on related compounds such as (Me₂N)_nPCl_{3-n} (*n* = 1—3) and R₂NPF₂ (R = Me or Et). The measurement of the He(I) photoelectron spectra of a complete series of similar compounds enables many of the

⁹ (a) J. L. Beauchamp, *Ann. Rev. Phys. Chem.*, 1971, **22**, 527; (b) R. V. Hodges and J. L. Beauchamp, *Inorg. Chem.*, 1975, **14**, 2887; (c) M. F. Lappert, J. B. Pedley, B. T. Wilkins, O. Stelzer, and E. Unger, *J.C.S. Dalton*, 1975, 1207; (d) O. Stelzer and E. Unger, *Chem. Ber.*, 1975, **108**, 1246; (e) D. C. Mente and J. L. Mills, *Inorg. Chem.*, 1975, **14**, 1862; (f) L. J. V. Griend and J. G. Verkade, *J. Amer. Chem. Soc.*, 1975, **97**, 5960; (g) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, 1975, **14**, 2224; (h) R. Savoie and P. A. Giguère, *J. Chem. Phys.*, 1964, **40**, 2698; (i) K. O. Christe, *Inorg. Chem.*, 1975, **14**, 2230, 2821; (j) S. P. Mishra, M. C. R. Symons, K. O. Christe, R. D. Wilson, and R. I. Wagner, *Inorg. Chem.*, 1975, **14**, 1103.

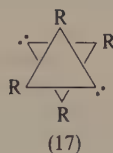
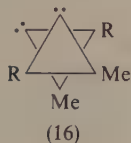
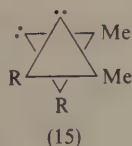
complexities which result from band overlap to be resolved so that a detailed picture of molecular orbital energies may be built up. The first band in the p.e. spectrum is assigned to the phosphorus lone pair and, by plotting the values of the corresponding ionization potential against parameters such as $^1J(\text{PB})$ in phosphine-borane complexes or the A_1 carbonyl-stretching frequencies in complexes *cis*-[MoL₂(CO)₄],^{9d} the conclusion is reached that the lone-pair ionization potential provides a good measure of relative basicities within a related series. Correlations with Hammett constants $\Sigma\sigma^{\text{Ph}}$ or $\Sigma\sigma_I^{\text{Ph}}$ are less clear (except for alkyl phosphines R_{3-n}PH_n). One of the attractions in using ionization potential data from p.e. spectra as a measure of basicity is that information may be obtained about a very wide range of compounds. The basicity of the trimethyl derivatives of the Group V elements towards a series of boron Lewis acids has been studied by classical methods. The expected trends in complex stability have been confirmed.^{9e}

One of the manifestations of amine and phosphine basicity is in the ready formation of onium salts in acidic media, and interest in these continues. For example, in solutions, usually in liquid sulphur dioxide, containing HSO₃F-SbF₅ and phosphorus halides, the species PHF₃⁺, PHF₂Cl⁺, PHCl₃⁺, PHCl₂Br⁺, PHClBr₂⁺, and PHBr₃⁺ have been identified by their ³¹P n.m.r. spectra, from which one-bond P-H coupling constants may be clearly measured.^{9f} The spectrum of PHF₃⁺, for example, shows a doublet of quartets with $^1J(\text{PH}) = 1190.6$ Hz. The new salts OH₃⁺[EF₆]⁻ (E = As or Sb), obtained as well-defined crystalline solids from the H₂O-HF-EF₅ system,^{9g} appear to be the most stable oxonium salts known and the most suitable for detailed study of the cation. Thus OH₃⁺[SbF₆]⁻ decomposes only above 350 °C. X-Ray powder data suggest that OH₃⁺[AsF₆]⁻ has a structure similar to that of Ag⁺[AsF₆]⁻ and that OH₃⁺[SbF₆]⁻ is similar to KMF₆ (M = Re, W, or Mo). The i.r. spectra of the cations are assigned by comparison with the isoelectronic ammonia; the bands are somewhat affected by cation-anion interactions, but much less so than those of mineral acid hydrates such as H₃O⁺ClO₄⁻.^{9h} The sulphonium salt SH₃⁺[SbF₆]⁻ was made similarly by condensing hydrogen sulphide on to a frozen solution of SbF₅ in HF, but attempts to make SH₃⁺[AsF₆]⁻ were not successful: hydrogen sulphide reacted quantitatively with arsenic(v) fluoride to give arsenic(v) sulphide.⁹ⁱ By careful experiments it was possible to obtain both i.r. and Raman spectra of the cation SH₃⁺ and to assign peaks by comparison with the isoelectronic PH₃. The peaks are much better defined than those of OH₃⁺. Protonation of HCl was also almost certainly achieved in HF-SbF₅ but the white solid adduct decomposed below room temperature and so full characterization of the cation was not possible.

Attempts to make the analogous NHF₃⁺ salts from NF₃ and SbF₅-HF were apparently unsuccessful, and starting material was recovered from the reaction mixture at -78 °C.⁹ⁱ The difluoroammonium cation NH₂F₂⁺ was, however, isolated in hexafluoro-antimonate(v) or -arsenate(v) salts, and, in spite of frequent explosions, n.m.r., i.r., and Raman data were recorded. The n.m.r. parameters for the NF₂H₂⁺ ion are in good agreement with those already formed for ions in the series NH₄⁺, NH₃F⁺, and NF₄⁺, and the vibrational spectra (except for solid-state effects) were assigned by comparison with CH₂F₂. The dangerous instability of the difluoroammonium salts at room temperature was attributed to exothermic elimination of hydrogen fluoride. Irradiation of NF₄⁺[AsF₆]⁻ and NF₄⁺[SbF₆]⁻ with ⁶⁰Co γ-rays gave samples with e.s.r. signals assigned to the NF₃⁺ radical cation.^{9j}

■ Diphosphines

Conditions have been described^{10a} for the synthesis of diphosphine, H_2PPH_2 , in *ca.* 30% yield by passing phosphine through an electric discharge. This seems to be an improvement on the more usual method, from the hydrolysis of calcium phosphide, which gives unpredictable yields. Methylphosphine, under similar conditions, gives the new diphosphines MePPH_2 and MePPHMe . Methyl diphosphine was thermally unstable and could not be isolated pure but its formation was clearly characterized by n.m.r. spectroscopy. 1,2-Dimethyldiphosphine was apparently formed as two diastereoisomers (15 and 16; $\text{R} = \text{H}$) with a *gauche* conformation. When a mixture of phosphine and acetylene was passed through the discharge, small amounts of buta-1,3-diyne, $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$, and the new compound ethynylphosphine, $\text{HC}\equiv\text{CPH}_2$, (yield 9%) were found. Isolation of these products is interesting since their formation involves the breaking of the $\text{H}-\text{C}$ bonds in acetylene.



The factors which determine the conformations of diphosphines are still not clear. Analysis^{10b} of the vibrational spectra of H_2PPH_2 in gas, liquid, and solid phases suggests that the only conformation is *gauche*; the microwave study described in 1974^{10c} was ambiguous on this point since any *trans*-isomer (17; $\text{R} = \text{H}$) would have no dipole moment and so be undetected. The hydrogen atoms in diphosphine appear to be too far apart to have much effect on the conformation, which must be dominated by lone-pair interactions. Further evidence for the predominantly *trans* conformation (17) in P_2F_4 and $\text{P}_2(\text{CF}_3)_4$ has been obtained from electron diffraction studies:^{10d} the $\text{P}-\text{P}$ distance in P_2F_4 (2.281 Å) is the longest yet determined. There is clearly no evidence for π -delocalization across the $\text{P}-\text{P}$ bond, in contrast to the situation in molecules such as Me_2NPF_2 or H_2NPF_2 , where the $\text{P}-\text{N}$ bonds are short. It is strange that, although the $\text{N}-\text{C}$ bonds in $\text{N}_2(\text{CF}_3)_4$ are comparable with those in other amines, the $\text{P}-\text{C}$ bonds in $\text{P}_2(\text{CF}_3)_4$ are longer [1.914(4) Å] than in most phosphines. Trends in bond lengths and angles in diphosphines (Table 4) cannot be predicted by VSEPR theory, which suggests that angles adjacent to more electronegative substituents should be decreased.

Table 4 Structural parameters for diphosphines P_2X_4

| X | $\text{P}-\text{P}/\text{\AA}$ | $\angle\text{PPX}/^\circ$ | $\angle\text{XPX}/^\circ$ |
|---------------|--------------------------------|---------------------------|---------------------------|
| Me | 2.192(9) | 101.1(7) | 99.6(10) |
| H | 2.218(4) | 95.2(6) | 91.3(14) |
| CF_3 | 2.182(16) | 106.7(7) | 103.8(8) |
| F | 2.281(6) | 95.4(3) | 99.1(4) |

¹⁰ (a) J. P. Albrand, S. P. Anderson, H. Goldwhite, and L. Huff, *Inorg. Chem.*, 1975, **14**, 570; (b) J. D. Odom, C. J. Wurrey, L. A. Carreira, and J. R. Durig, *Inorg. Chem.*, 1975, **14**, 2849; (c) J. R. Durig, L. A. Carreira, and J. D. Odom, *J. Amer. Chem. Soc.*, 1974, **96**, 2688; (d) H. L. Hodges, L. S. Su, and L. S. Bartell, *Inorg. Chem.*, 1975, **14**, 599 and references therein; (e) H. C. E. McFarlane and W. McFarlane, *J.C.S. Chem. Comm.*, 1975, 582; (f) R. K. Harris, E. M. McVicker, and M. Fild, *J.C.S. Chem. Comm.*, 1975, 886; (g) G. R. Newkome, J. D. Sauer, and M. L. Erbland, *J.C.S. Chem. Comm.*, 1975, 885.

Conformations in diphosphines have also been investigated by n.m.r. spectroscopy. An analysis of the spectra of $\text{Bu}^t\text{MePPMeBu}^t$ indicated that only the *gauche*-isomer with the conformation (16; $\text{R} = \text{Bu}^t$) was present in appreciable concentrations at the temperatures studied.^{10e} Replacement of methyl by *t*-butyl groups gives a much more negative value for the coupling constant $^1J(\text{PP})$ and it has been suggested that this indicates a change in hybridization at phosphorus with an increase in the CPC angle and an increase in *s*-character of the P—P bond. It has also been shown^{10f} that in diphosphines $\text{R}^1\text{R}^2\text{PPR}^1\text{R}^2$ the parameter $[^1J(\text{PC}) + ^2J(\text{PCC})]$, which is easily found from the ^{13}C n.m.r. spectrum, may be used to assign conformations. For the series $(\text{MeEtP})_2$, $(\text{MePr}^i\text{P})_2$, and $(\text{MeBu}^t\text{P})_2$, the proportion of the *meso*-diastereoisomer (15) (in which the larger groups cannot adopt a *trans* configuration) relative to the racemic (16) decreases, showing the effect of steric interactions between the larger groups.

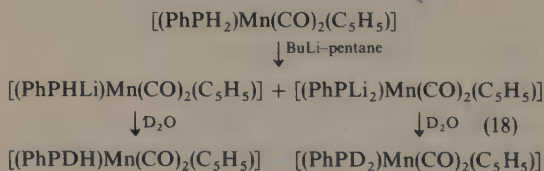
A new preparation of diphosphorus tetraiodide, in 75–80% yield from potassium iodide and phosphorus(III) chloride, has been described.^{10g}

9 Methylidynephosphine

Modern instrumentation allows detailed data to be obtained on short-lived species. Methylidynephosphine, HCP, which may be obtained by passing phosphine at low pressure through a carbon arc, rapidly polymerizes above -70°C . If, however, the gaseous reaction products, with or without vinyl chloride as solvent, are condensed at -100°C , the n.m.r. spectrum may be recorded at that temperature.^{11a} The value of $^1J(^{13}\text{CH})$ (211 Hz) is in the range expected for $\text{C}(\text{sp})\text{—H}$ bonds and $^2J(\text{HCP})$ (43.9 Hz) is much larger than is normally found in phosphines or phosphonium salts. These results are consistent with the proposal that the molecule in solution is best described by the structure $\text{HC}^{\delta-}\equiv\text{P}^{\delta+}$, as suggested by earlier microwave data.^{11b}

10 Phosphinidene and Arsinidene Complexes

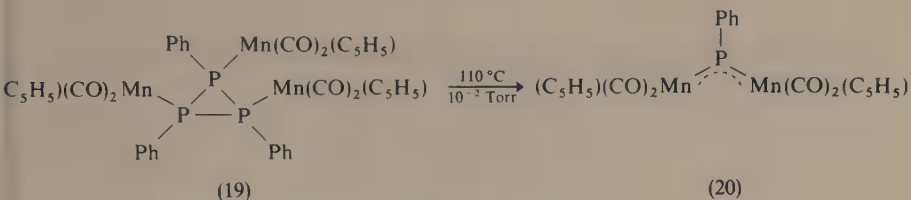
A number of phosphine complexes may be metallated by butyl-lithium to give yellow crystalline lithio-derivatives as indicated in Scheme 2.^{12a} These compounds may be kept as solids for several days, but they are sensitive towards moisture and are pyrophoric, and decompose even at -20°C in THF or dioxan. The dilithiophosphine complex (18) reacts^{12b} with *NN*-dichlorocyclohexylamine to give the red



Scheme 2

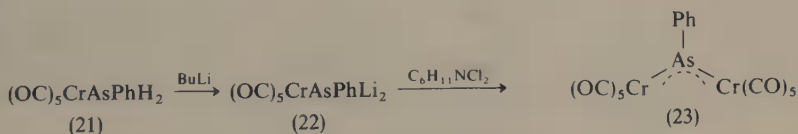
¹¹ (a) S. P. Anderson, H. Goldwhite, D. Ko, A. Letsou, and F. Esparza, *J. C.S. Chem. Comm.*, 1975, 744; (b) J. K. Tyler, *J. Chem. Phys.*, 1964, **40**, 1170.

¹² (a) G. Huttner and H.-D. Müller, *Z. Naturforsch.*, 1975, **30b**, 235; (b) G. Huttner, H.-D. Müller, A. Frank, and H. Lorenz, *Angew. Chem. Internat. Edn.*, 1975, **14**, 572; (c) M. Baudler and M. Bock, *Z. anorg. Chem.*, 1973, **395**, 37; (d) G. Huttner, H.-D. Müller, A. Frank, and H. Lorenz, *Angew. Chem. Internat. Edn.*, 1975, **14**, 705; (e) G. Huttner and H.-G. Schmid, *Angew. Chem. Internat. Edn.*, 1975, **14**, 433; G. Huttner, J. V. Seyerl, M. Marsili, and H.-G. Schmid, *ibid.*, p. 434.



compound $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{MnPPh}]_3$ (19) and this has been shown by an X-ray study to contain the ligand $(\text{PPh})_3$. Free triphenylcyclotriphosphine may be isolated^{12c} but it rearranges above -20°C to the pentaphosphine $(\text{PhP})_5$. The complex $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{MnPPh}]_3$ is stable in air. It decomposes on heating to give a new compound $\text{PhP}[\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ (20); the X-ray structure shows that the co-ordination at phosphorus is planar and the $\text{Mn}-\text{P}$ bonds ($2.184 \pm 0.002 \text{ \AA}$) are unusually short (*cf.* $2.26-2.40 \text{ \AA}$ in Mn-phosphine complexes). The compound thus appears to be the first example of planar phosphorus in which electrons from the manganese are used to complete the valence shell.

A similar complex of arsenic has been isolated. The phenylarsine complex (21) may be metallated with *n*-butyl-lithium and the resulting dilithio-derivative (22) reacts with *NN*-dichlorocyclohexylamine to give the intensely coloured arsinidene complex $\text{PhAs}[\text{Cr}(\text{CO})_5]_2$ (23). An X-ray study shows that the co-ordination at arsenic is planar and that the $\text{As}-\text{Cr}$ bonds (2.38 \AA) are short compared with those



in R_3As complexes. The $\text{Mn} \cdots \text{P} \cdots \text{Mn}$ groups in (20) and $\text{Cr} \cdots \text{As} \cdots \text{Cr}$ group in (23) may be described as three-centre 4π -systems; the intense ($\epsilon = 20\,000$) absorption involving charge transfer from metal to ligand is then ascribed to the ${}^1\text{A}_1 \rightarrow {}^1\text{B}_2$ transition (Figure 1).

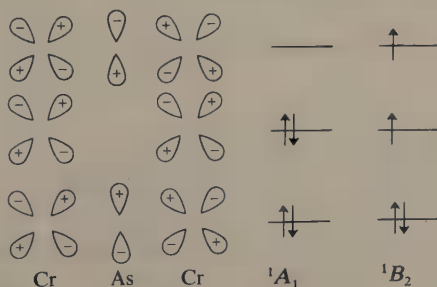
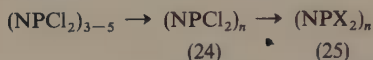


Figure 1 Molecular orbital diagram for the arsinidene complex $\text{PhAs}[\text{Cr}(\text{CO})_5]_2$

11 Phosphazenes

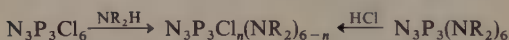
After the silicones, the phosphazenes constitute the most important group of polymers based on inorganic backbones.^{13a}

The P—Cl bond in polydichlorophosphazene (24) is hydrolytically unstable, but high molecular weight polymers (NPX₂)_n (25; e.g., X = OPh or OCH₂CF₃) have

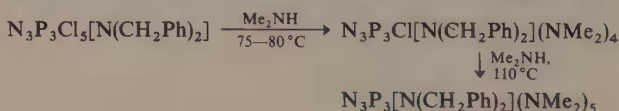


important uses as elastomers or water repellants. These materials, which cannot be made by direct polymerization of cyclic (NPX₂)₃₋₅, are accessible by nucleophilic substitution reactions on polydichlorophosphazene. Substitution, however, is more simply studied in cyclic derivatives; for example, the reaction between (NPCI₂)₃ and sodium 2,2,2-trifluoroethoxide has yielded the first complete set of products N₃P₃Cl_n(OR)_{6-n} (R = CH₂CF₃, n = 0–6).^{13b} Successive substitution is non-geminal and *trans*, and the sequence of reactions appears to be determined mainly by steric factors. Substitution reactions of *ortho*-diphenols, however, may lead to degradation of P—N rings; it is thought that the introduction of a five-membered exocyclic ring, as in the undetected (26), increases the susceptibility of the N₃P₃ ring to nucleophilic attack, as the steric strain is relieved with formation of phosphoranes such as (27) or (28). Support for this suggestion comes from the isolation of the intermediate (27) from the reaction between N₃P₃Cl₆ and *o*-aminophenol.^{13c} Reactions are complicated by scrambling of cyclic ligands during the degradation.

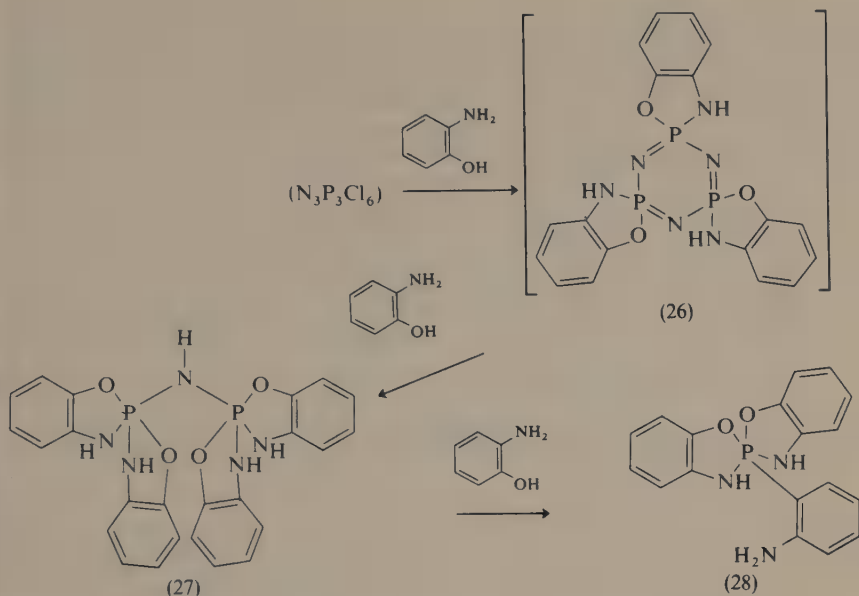
Many derivatives N₃P₃X_n(NR₂)_{6-n} (X = halogen) have been made either by the reaction between hexachlorocyclotriphosphazene and amines or by treatment of the hexakisamido-derivatives N₃P₃(NR₂)₆ with hydrogen halides:^{13d}



The importance of steric effects in shielding chlorine atoms from nucleophilic attack by amine has been illustrated by isolation of the compound N₃P₃Cl[N(CH₂Ph)₂](NMe₂)₄ from the reaction between N₃P₃Cl₅N(CH₂Ph)₂ and dimethylamine in toluene;^{13e} in many aminations the final chlorine is rapidly displaced with formation of the hexakisamido-derivative, but forcing conditions are required here,

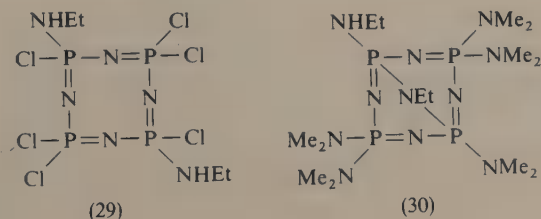


¹³ (a) H. R. Allcock, *Chem. Rev.*, 1972, **72**, 315; *Chem. in Britain*, 1974, **10**, 118; (b) J. L. Schmutz and H. R. Allcock, *Inorg. Chem.*, 1975, **14**, 2433; (c) H. R. Allcock, R. L. Kugel, and G. Y. Moore, *Inorg. Chem.*, 1975, **14**, 2831; (d) S. N. Nabi, R. A. Shaw, and C. Stratton, *J.C.S. Dalton*, 1975, 588; (e) Masood-ul-Hasan, R. A. Shaw, and M. Woods, *J.C.S. Dalton*, 1975, 2202; (f) T. S. Cameron, K. Mannan, S. S. Krishnamurthy, A. C. Sau, A. R. V. Murthy, R. A. Shaw, and M. Woods, *J.C.S. Chem. Comm.*, 1975, 975; (g) D. W. J. Cruickshank, *Acta Cryst.*, 1964, **17**, 671; (h) H. T. Searle, J. Dyson, T. N. Ranganathan, and N. L. Paddock, *J.C.S. Dalton*, 1975, 203; (i) H. P. Calhoun and J. Trotter, *J.C.S. Dalton*, 1974, 377, 382; (j) H. P. Calhoun, R. H. Lindstrom, R. T. Oakley, N. L. Paddock, and S. M. Todd, *J.C.S. Chem. Comm.*, 1975, 343; (k) H. P. Calhoun, R. T. Oakley, and N. L. Paddock, *J.C.S. Chem. Comm.*, 1975, 454; (l) O. J. Scherrer and N. Kuhn, *Chem. Ber.*, 1974, **107**, 2123; R. Appel and M. Halstenberg, *J. Organometallic Chem.*, 1975, **99**, C25.



The reaction between hexachlorobis(ethylamino)cyclotetraphosphazene (29) and an excess of dimethylamine yields, among other products, the unusual bicyclic phosphazene $\text{N}_4\text{P}_4(\text{NMe}_2)_5(\text{NHEt})(\text{NEt})$ (30).^{13f} The P—N bonds in the ring (mean 1.602 Å) are comparable with those in other phosphazene rings in which the bond order is considered to be greater than one. The P—N bonds at the bridgehead, however, appear to be inequivalent; the longer bond has a length (1.77 Å) comparable with that in sodium phosphoramidate^{13g} (1.769 Å), which is normally considered to be a P—N single bond.

A further group of phosphazenes may be obtained by replacement of the chlorine atoms in chlorophosphazenes by alkyl or aryl groups. These phosphazenes are characterized by longer P—N bonds and greater charge localization, so that the nitrogen atoms become basic.^{13h} Thus the cyclic methylphosphazenes $(\text{NPMe}_2)_{3-5}$ form salts such as $\text{N}_3\text{P}_3\text{Me}_6\cdot\text{HCl}$, $\text{N}_4\text{P}_4\text{Me}_8\cdot 2\text{HClO}_4$, and $\text{N}_5\text{P}_5\text{Me}_{10}\cdot\text{H}_2\text{CuCl}_4\cdot\text{H}_2\text{O}$ or complexes such as $\text{N}_4\text{P}_4\text{Me}_8\cdot 2\text{HgCl}_2$, $\text{N}_4\text{P}_4\text{Me}_8\cdot 4\text{AgNO}_3$, and $\text{N}_4\text{P}_4\text{Me}_8\cdot\text{HCl}\cdot\text{CuCl}_2$. All three phosphazenes form quaternary salts $\text{N}_n\text{P}_n\text{Me}_{2n}\text{RI}$ ($n = 3-5$; $\text{R} = \text{Me}$ or Et) with iodoalkanes. The properties of these alkylphosphazenes are attributed to the less electronegative substituents at



phosphorus so that the *d*-orbitals are more diffuse than in the halogenophosphazenes and less suited to overlap with nitrogen *p*-orbitals. Some of the structural information^{13*h,i*} on protonated or quaternized phosphazenes is shown in Figure 2. The high-energy of the allowed transition at *ca.* 190 nm, associated with ring electrons, confirms that the phosphorus and nitrogen orbitals have appreciably different electronegativities.

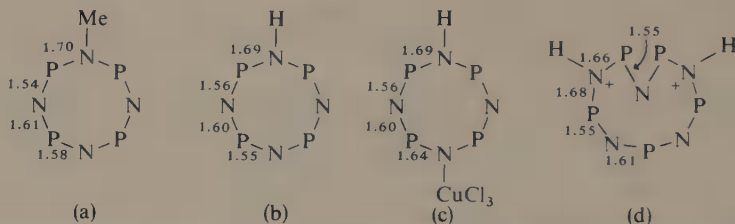
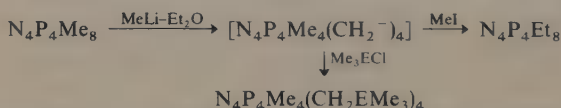
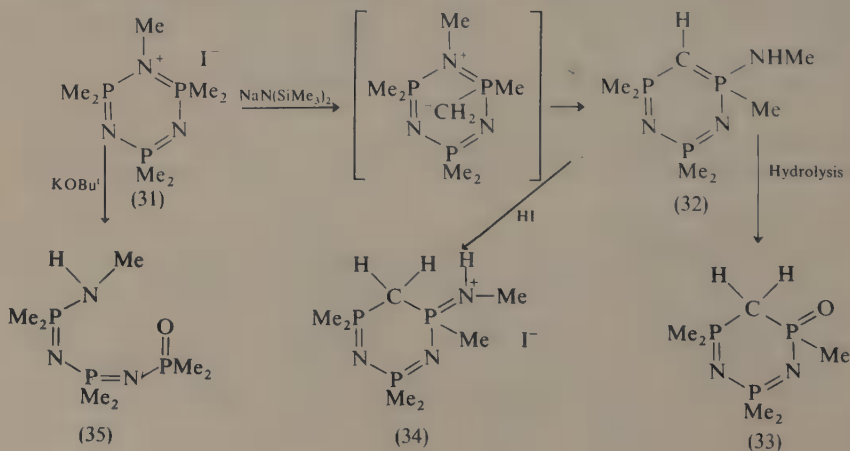


Figure 2 Mean bond lengths (Å) in (a) $\text{N}_4\text{P}_4\text{Me}_9^+$, (b) $\text{N}_4\text{P}_4\text{Me}_8\text{H}^+$, (c) $\text{N}_4\text{P}_4\text{Me}_8\text{H}^+\text{CuCl}_3$, and (d) $\text{N}_5\text{P}_5\text{Me}_{10}\text{H}_2^{2+}$

The reaction between octamethylcyclophosphazene and methyl-lithium in dimethyl ether gives the new carbanion $[\text{N}_4\text{P}_4\text{Me}_4(\text{CH}_2^-)_4]$ which has been identified by its reactions with iodomethane and the halides Me_3EX ($\text{E} = \text{Si}, \text{Ge}, \text{or Sn}$).^{13*j*}

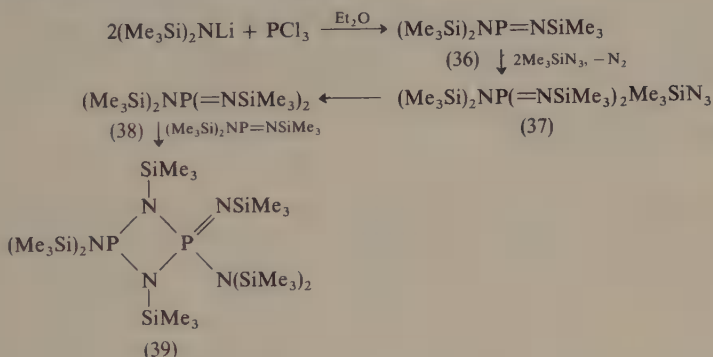


Deprotonation occurs at *P*-methyl rather than at *N*-methyl groups, and it is thought that the carbanion may be stabilized by conjugation within the π -system of the ring. Deprotonation of *N*-phosphazanium iodides is more complicated.^{13*k*} Thus the compound $\text{P}_3\text{N}_3\text{Me}_7\text{I}$ (31) reacts with sodium bis(trimethylsilyl)amide to give the ylidic diazaphosphorin (32), confirmed by hydrolysis to the phosphine oxide (33) and protonation to the *C*-hydride (34).



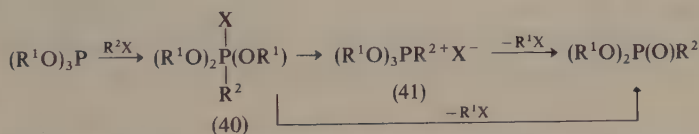
The initial step in the reaction appears to be deprotonation at a *P*-methyl group as in the phosphazenes. With potassium *t*-butoxide, however, the phosphazanium iodide (31) is converted into a linear phosphine oxide (35) by a process which appears to involve nucleophilic attack of *t*-butoxide on phosphorus, followed by elimination of isobutene.

The reaction between lithium bis(trimethylsilyl)amide and phosphorus(III) halides gives 50–70% yields of the iminophosphine $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$ (36).¹³¹ This compound, which is very reactive towards air or moisture, may be converted into a 1:1 adduct (37) with trimethylsilyl azide, and, on distillation, the bisiminophosphorane $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)_2$ (38) is obtained. This may then be treated with more of the iminophosphine to give a four-membered ring compound (39) with both tervalent and quinquevalent phosphorus.



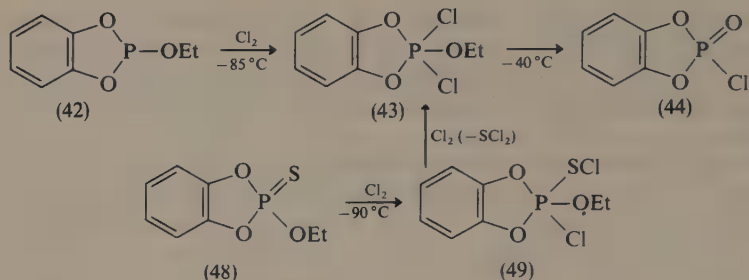
12 Reactions of Phosphorus Esters

More experiments to identify intermediates in the conversion of phosphites into phosphonates by alkyl halides or halogens have been described. In earlier studies, much information was obtained by use of optically active compounds.^{14a} The

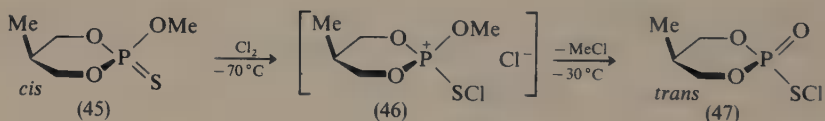


observed stereospecificity, which depends on the groups R^1 and R^2 , is thought to be a function of the lifetime of the five-co-ordinate intermediate (40). If this is short and alkyl halide R^1X is rapidly eliminated, either directly or *via* a phosphonium salt (41), optical purity is maintained; if the five-co-ordinate intermediate persists long enough to allow pseudorotation, optical purity is lost. Five-co-ordinate species may be stabilized in cyclic phosphites [e.g. (42)]. Intermediates in Arbuzov-type reactions have now been detected directly^{14b} by ^{31}P n.m.r. spectra of samples at -85°C in chloroethane solution. The peak due to the five-co-ordinate intermediate (43)

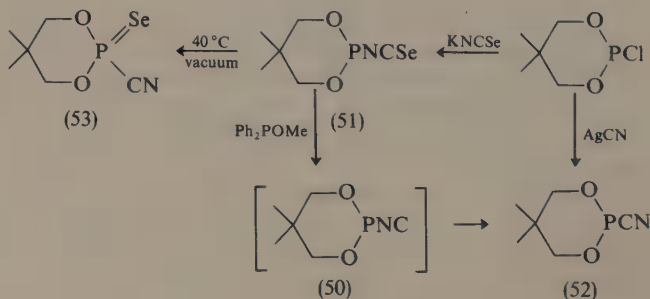
¹⁴ (a) C. L. Bodkin and P. Simpson, *J.C.S. Perkin II*, 1972, 2049; (b) A. Skowrońska, J. Mikołajczak, and J. Michalski, *J.C.S. Chem. Comm.*, 1975, 791, 986; (c) W. J. Stec, T. Sudoł, and B. Uznański, *J.C.S. Chem. Comm.*, 1975, 467.



weakens when the sample is warmed to -40°C and a new peak corresponding to the phosphorochloridate product (44) appears. Both phosphonium and five-co-ordinate intermediates have been detected in chlorinations of phosphorus thioesters. The *cis*-cyclic thionate (45) is converted *via* the phosphonium intermediate (46) into the *trans*-sulphenyl chloride (47) with full retention of configuration. Chlorination of the five-membered cyclic phosphorothionate (48) proceeds *via* five-co-ordinate intermediates (49) and (43).



The easy rearrangement of the isocyano-derivative $\text{Me}_2\text{C}(\text{CH}_2\text{O})_2\text{P}(\text{O})\text{NC}$ to the corresponding cyano-compound was described last year. The prediction that the corresponding isocyano-derivative of trivalent phosphorus (50) should rearrange even more easily has been confirmed,^{14c} since attempts to isolate the compound from the deselenization of the isoselenocyanate compound (51) by reaction with methyl diphenylphosphinite, Ph_2POMe , yielded only the cyano-compound (52). The crude compound obtained from $\text{Me}_2\text{C}(\text{CH}_2\text{O})_2\text{P}(\text{O})\text{NC}$ and potassium isoselenocyanate was used in the deselenization reaction, since attempts to distil the compound $\text{Me}_2\text{C}(\text{CH}_2\text{O})_2\text{PNCSe}$ gave only the rearranged product (53).



PART IV: Groups VI—VIII

By R. H. Cragg

1 Group VI

During 1975 a considerable amount of work has been published concerning the chemistry and properties of compounds of the Group VI elements. Two major areas which merit special mention are (i) the continuing interest in 'crown' ethers and (ii) the synthesis and properties of organic polymers, such as $(\text{SN})_n$, which have metallic properties.

A major characteristic of crown ethers is their ability to stabilize anions. For example dibenzo-18-crown-6 and 18-crown-6 ethers have been reported to facilitate a simple and direct route to anionic derivatives of Group VI metal hexacarbonyls.¹ The crown ether- $[\text{W}(\text{CO})_5\text{OH}]^-$ compound is obtained in 57% yield from a mixture of hexacarbonyltungsten, crown ether, and potassium hydroxide in methylene dichloride which has been irradiated for two hours using a mercury lamp. The analogous fluoride compound is obtained in 27% yield by substituting potassium fluoride for the hydroxide. However, if tetraethylammonium fluoride is used, only 7% of the anion is obtained. Other complex anions reported are $[\text{M}(\text{CO})_5\text{X}]^-$ ($\text{M} = \text{Cr}$, $\text{X} = \text{F}$ or OH). One of the major problems in the development of the properties of crown ethers has been the lack of a convenient method of synthesis. However, recently, optically pure, configurationally chiral 18-crown-6 and 9-crown-3 cryptands have been synthesized from L-tartaric acid and D-mannitol.² In order to obtain an assessment of the complexing power of the 18-crown-6 derivatives, the stability constants, defined as equilibrium constants (K in l mol^{-1}) for the equilibrium



have been measured for metal and primary alkylammonium cations. The results, given in Table 1, indicate that the 18-crown-6 cryptands form strong cationic constants, defined as equilibrium constants (K in l mol^{-1}) for the equilibrium

Table 1 Stability constants for cryptate complexes

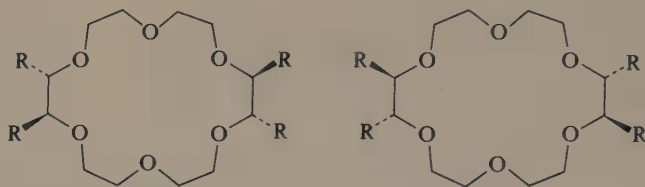
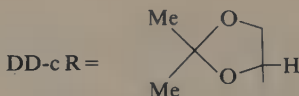
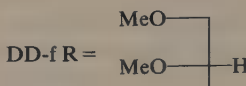
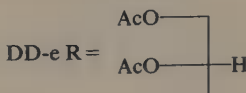
| Cryptate | K | Cryptate | K |
|-----------------------------------|---------------------|--------------------|-------------------|
| LL-a Bu^tNH_3^+ | 2×10^4 | DD-c Na^+ | 3.9×10^3 |
| LL-b Bu^tNH_3^+ | $< 1.0 \times 10^4$ | DD-c K^+ | 3.0×10^4 |
| DD-c Bu^tNH_3^+ | < 30 | DD-c Rb^+ | 4.6×10^4 |
| DD-c $\text{PhCH}_2\text{NH}_3^+$ | 1.5×10^6 | | |

One important property of these crown ethers is their ability to differentiate in complex equilibria between $(\pm)(\text{RS})$ - α -phenylethylammonium hexafluorophosphate.³ This is observed when the substituent groups on the configurationally chiral

¹ J. L. Cihonskii and R. A. Levenson, *Inorg. Chem.*, 1975, **14**, 1717.

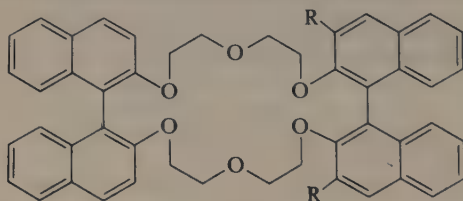
² W. D. Curtis, D. A. Laidler, J. F. Stoddart, and G. H. Jones, *J.C.S. Chem. Comm.*, 1975, 833.

³ W. D. Curtis, D. A. Laidler, J. F. Stoddart, and G. H. Jones, *J.C.S. Chem. Comm.*, 1975, 835.

LL-a R = CH₂OCH₂PhLL-b R = CH₂OCPh₃LL-d R = CH₂OAcDD-d R = CH₂OAc**Figure**

18-crown-6 cycle are bulky. For example host (*S*)-LL-b HPF₆ is *ca.* 1.00 kJ mol⁻¹ more stable than (*R*)-LL-b HPF₆. In contrast (*R*)-DD-c HPF₆ is *ca.* 1.25 kJ mol⁻¹ more stable than the (*S*)-DD-c HPF₆ complex.

The important property of crown ethers in chiral recognition has been further extended. The cyclic ether (1), containing two 2,2'-substituted-1,1'-binaphthyl units as chiral barrier, has been synthesized and observed to complex somewhat selectively the enantiomers of the hexafluorophosphate salt of racemic methyl phenylglycinate.⁴



(1) R = H or Me

Analogous macrocyclic ethers (2) are observed to complex differently with the enantiomers of the hexafluorophosphate salts of racemic methyl phenylglycinate or methyl valinate.⁵

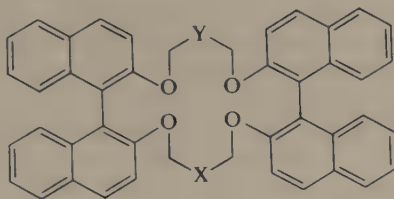
Compounds (3) or (4) are obtained by condensation of a diaza-18-crown-6 ether with an acid chloride, followed by reduction with diborane of the resulting cyclic diamide,⁶ and have been found to catalyse nucleophilic substitution reactions as well

⁴ G. W. Gokel, J. M. Timko, and D. J. Cram, *J.C.S. Chem. Comm.*, 1975, 394.

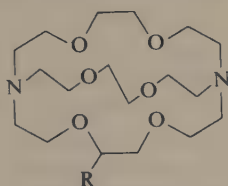
⁵ G. W. Gokel, J. M. Timko, and D. J. Cram, *J.C.S. Chem. Comm.*, 1975, 444.

⁶ M. Cinquini, F. Montanari, and P. Tundo, *J.C.S. Chem. Comm.*, 1975, 393.

as alkylation at carbon, cyclopropanation, and borohydride reduction. Table 2 gives some idea of the catalytic effect in the reaction of an alkyl bromide with potassium iodide.



- (2) e.g., $X = Y = \text{CH}_2\text{OCH}_2$
 $X = \text{CH}_2\text{OCH}_2$, $Y = \text{CH}_2\text{CH}_2\text{CH}_2$



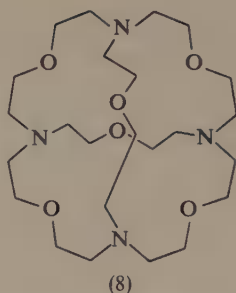
- (3) $R = n\text{-C}_{14}\text{H}_{29}$
 (4) $R = n\text{-C}_{11}\text{H}_{23}$
 (5) $R = \text{H}$
 (6) $n\text{-C}_{16}\text{H}_{33}^+\text{P}^+\text{Bu}_3\text{Br}^-$
 (7) crown ether

Table 2 Relative catalytic effects of the compounds (3)–(7) in the reaction
 $n\text{-C}_8\text{H}_{17}\text{Br} + \text{KI} \rightarrow n\text{-C}_8\text{H}_{17}\text{I} + \text{KBr}$

| Catalyst | $T/^\circ\text{C}$ | Reaction time/h | Yield of $n\text{-C}_8\text{H}_{17}\text{I}$ (%) |
|----------|--------------------|-----------------|---|
| (3) | 60 | 0.2 | 100 |
| (4) | 60 | 0.5 | 92 |
| (5) | 60 | 14 | 90 |
| (6) | 60 | 1 | 93 |
| (7) | 80 | 3 | 100 |

The molecular recognition of the spherical alkali- or alkaline-earth cations by an organic ligand should ideally be achieved by a system containing a spherical intramolecular cavity into which the cation may be included. Recently the macrocyclic system (8) has been synthesized.⁷ When solid CsBr is added to a CDCl_3 solution of (8), the salt dissolves slowly and the initial n.m.r. spectrum is slowly replaced by a new spectrum of the 1:1 complex. Complex formation is also observed by n.m.r. with KBr , CsBr , or BaBr_2 in D_2O , as well as with NH_4I in CDCl_3 . As all the bridges in the ligand are equivalent in the exchanging complex in CDCl_3 , the complex must have a centre of symmetry. This strongly suggests that the cation is trapped inside the cavity of the ligand. The cryptate has a cavity radius of about 1.8 Å and its high connectivity introduces considerable rigidity in the molecule.

⁷ E. Graf and J. M. Lehn, *J. Amer. Chem. Soc.*, 1975, **97**, 5022.



Preliminary measurements show that the stability constants for the K^+ , Rb^+ , and Cs^+ complexes are about 3.4, 4.2, and 3.4, respectively ($\log k_s$ in water at 25 °C), and the Cs^+ complex is probably the most stable to date. The cation exchange rates (determined from 1H n.m.r. coalescence temperatures) are amongst the lowest observed, with free energies of activation of 64.8 (at 28 °C), 69.8 (51 °C), and 67.3 (41 °C) kJ mol^{-1} for the K^+ , Rb^+ and Cs^+ complexes, respectively.

The structures of a number of crown ethers have been reported. *X*-Ray diffraction studies of two of the five possible isomers of dicyclohexyl-18-crown-6 show that the oxygen atoms lie approximately in a plane with the cavity elliptical in shape and the shorter distance across the ellipse slightly more than 4 Å.⁸ In both isomers, the cavity surrounded by the six oxygen atoms is elliptical in shape with the two axial oxygen atoms pointing out of the cavity.

The structures of three macrocyclic thioethers 1,4,7-trithia-(12-crown-4), 1,4-dithia-(15-crown-5), and 1,10-dithia-(18-crown-6), with ring sizes varying from 12 to 18 atoms, have been determined by *X*-ray diffraction, and the donor atoms have been found to be nearly coplanar with all the sulphur atoms directed out of the cavities.⁹ The oxygen atoms are directed into the cavities with the exception of one oxygen atom in the crown-5 compound. The average C—C distances in the ring are 1.49, 1.51, and 1.50 Å, shorter than the expected 1.54 Å.

Polyether antibiotics are important monocarboxylic acid isophores owing to their ability to solubilize cations and facilitate their passage through membranes. The absolute configuration and constitution of the polyether antibiotic RO21-6150 has been established by *X*-ray crystallographic analysis of the silver salt.¹⁰ The co-ordination about the silver ions is irregular with eight Ag—O contacts which are less than 3.01 Å.

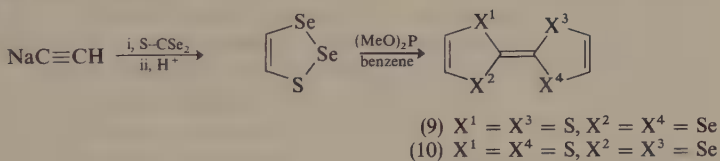
Carbon-based polymers, such as polyacetylene, are known to exhibit electrical insulating properties. In contrast, it has recently been recognized that polymers containing sulphur and nitrogen, or sulphur and selenium, often have properties similar to those of a metal. The observation of superconducting phenomena in the fluctuation region in the 'organic metal' tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) has aroused considerable interest in the use of π -donors with TCNQ, in the hope of obtaining new 'organic metals'. Recently, the

⁸ N. K. Dalley, J. S. Smith, S. B. Larson, J. J. Christensen, and R. M. Izatt, *J.C.S. Chem. Comm.*, 1975, 43.

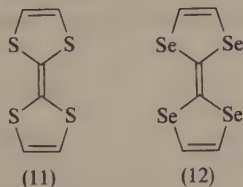
⁹ N. K. Dalley, J. S. Smith, S. B. Smith, S. B. Larson, K. L. Matheson, J. J. Christensen, and R. M. Izatt, *J.C.S. Chem. Comm.*, 1975, 84.

¹⁰ J. F. Blount, R. H. Evans, C. Liu, T. Hermann, and J. W. Westley, *J.C.S. Chem. Comm.*, 1975, 853.

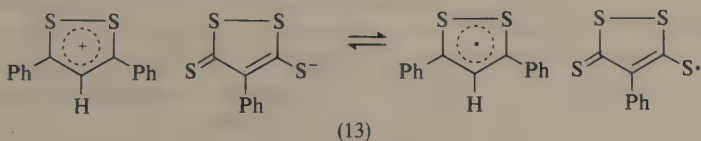
cis- (9) and *trans*-forms (10) of diselenadithiafulvalene (DSeDTF) have been reported, and on mixing with TCNQ in acetonitrile a black 1 : 1 charge-transfer salt is instantly precipitated.¹¹ Single-crystal electrical conductivity measurements show a metallic-like temperature dependence with a room-temperature conductivity of *ca.* $550 \Omega^{-1} \text{cm}^{-1}$. Charge-transfer salts containing the organic donor TTF or a derivative have the highest electrical conduction of organic solids presently known and it has been observed that the selenium analogue has led to an improvement in the metallic-like properties of its charge-transfer salt with TCNQ. Other workers have found the d.c. electrical conductivity to be $700 \pm 300 \Omega^{-1} \text{cm}^{-1}$ at room temperature; the conductivity has a negative temperature coefficient upon cooling.¹² The TCNQ salts of TTF and its selenium analogues form an isostructural series of highly conducting organic salts,¹³ having remarkably similar electrical conductivities with peaks at 59, 40, and 64 K, respectively.



The X-ray diffraction pattern and unit cell constants for the TCNQ salts of TTF (11), DSeDTF (9) and (10), and TSeF (12) show these three materials to be isostructural and the ^1H n.m.r. spectra show the presence of equal amounts of the *cis*- and *trans*-isomers in neutral DSeDTF.



Another organic system has been observed to have similar properties;¹⁴ 1,2-dithiolylum 5-thioxo-1,2-dithiole-3-thiolates have been observed to be charge-transfer salts with semiconducting electrical properties. The specific d.c. resistance ρ_{20} was *ca.* 10^7 – $10^8 \Omega \text{cm}^{-1}$ for 3,5-diphenyl-1,2-dithialylum 4-phenyl-5-thioxo-1,2-dithiole-3-thiolate (13). This is a little surprising, since the corresponding salts derived from 3-phenyl-1,2-dithiolylum salts and 3,4-diphenyl-1,2-dithiolylum salts were found to be insulators.



¹¹ E. M. Engler and V. V. Patel, *J.C.S. Chem. Comm.*, 1975, 671.

¹² M. V. Lakshmikantham, M. P. Cava, and A. F. Garito, *J.C.S. Chem. Comm.*, 1975, 383.

¹³ S. Etemad, T. Penney, E. M. Engler, B. A. Scott, and P. E. Seider, *Phys. Rev. Letters*, 1975, **34**, 741.

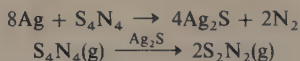
¹⁴ N. Loayza and C. T. Pedersen, *J.C.S. Chem. Comm.*, 1975, 496.

An all-valence-electron CNDO/2 MO calculation predicts that the boat form of cyclohexasulphur is the stable conformer and that its potential energy is *ca.* 16.7 kJ mol⁻¹ less than that of the chair form which is found in the rhombohedral crystals. The interconversion has a barrier of 96.1 kJ mol⁻¹.¹⁵

The crystal structures of Ba₂S₃ and BaS₃, determined from three-dimensional single-crystal X-ray diffraction data, show that the former contains a sulphide ion and an S₂²⁻ polysulphide ion with S—S distance 2.32 Å.¹⁶ In the latter, a polysulphide anion with S₃²⁻ has S—S 2.074 Å and an SSS angle of 114.8°. The Ba₂S₃ phase is apparently formed only at elevated temperature. The volume available per S atom by subtracting the volume of Ba²⁺ from the unit cell volumes of BaS, Ba₂S₃, and BaS₃ gives the values 54.84, 42.78, and 29.37 Å³, respectively. Thus at high pressures the formation of polysulphide anions is favoured because more of the available space is utilized by the S atoms.

Perhaps the most significant contribution to Group VI chemistry during 1975 has been the synthesis of analytically pure single crystals of the metallic conductor polymeric sulphur nitride (SN)_n, polythiazyl, in a convenient form for solid-state investigations.^{17,18} The significance of this work may be seen as an extension of the study of 'organic metals' and inorganic conductors, the electrical properties of which are quasi-one-dimensional, to potentially conducting polymeric materials.

Polymeric (SN)_n was first reported in 1910 but the potential of this polymer as a metallic conductor has only recently been recognized. This is because the intrinsic electronic properties of anisotropic solids are extremely sensitive to impurities and defects. Ultra-pure polythiazyl is obtained by the following method. The vapour of S₄N₄ is passed over heated silver wool, S₂N₂ collecting on the surface of a cold-finger containing liquid nitrogen. Polythiazyl is then obtained by slowly growing crystals, by



sublimation of S₂N₂ at 0 °C over a period of two days, followed by room-temperature solid-state polymerization over a period of three days, and then completing the polymerization by heating at 75 °C for two hours. During the formation of (SN)_n the colourless tabular monoclinic crystals of S₂N₂ turn dark blue and become paramagnetic (*g* = 2.005) and then change to gold, diamagnetic crystals which are pseudomorphous with, and have the same space group (*P*2₁/*c*) as, the S₂N₂ crystals from which they are obtained. The purity of (SN)_n can be confirmed by the fact that the polymer is diamagnetic, has not the characteristic iodine-like odour of S₂N₂ and there is no vapour pressure of S₂N₂ above the polymer at room temperature. Scanning electron micrographic studies indicate that the crystalline polymer is composed of an ordered array of parallel (SN)_n fibres. At room temperature, the d.c. conductivity is *ca.* 2.5 × 10³ Ω⁻¹ cm⁻¹ in a direction parallel to the fibre, and this value compares favourably with those obtained for metals such as mercury. The value of the conductivity is temperature-dependent, a characteristic property of a

¹⁵ Z. S. Herman and K. Weiss, *Inorg. Chem.*, 1975, **14**, 767.

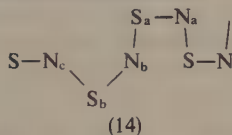
¹⁶ S. Yamaoka, J. T. Lemley, J. M. Jenks, and H. Steinfink, *Inorg. Chem.*, 1975, **14**, 129.

¹⁷ C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Amer. Chem. Soc.*, 1975, **97**, 6358.

¹⁸ A. G. MacDiarmid, C. M. Mikulski, P. J. Russo, M. S. Saran, A. F. Garito, and A. J. Heeger, *J.C.S. Chem. Comm.*, 1975, 476.

metal, and on decreasing the temperature to 10 K the conductivity increases *ca.* 225-fold. Indications that $(\text{SN})_n$ remains metallic at low temperature have been obtained from heat-capacity studies, and at 0.26 K $(\text{SN})_n$ is superconducting. Careful experimental technique is needed to obtain pure $(\text{SN})_n$ since the polymerization of S_2N_2 appears to take place at the surface of the crystals and consequently incompletely polymerized crystals can be obtained which appear to be identical with $(\text{SN})_n$ but have the same X-ray intensity data and cell dimensions of pure S_2N_2 . Although the polymer can be sublimed *in vacuo* at 140–150 °C, when heated above 208 °C or in an evacuated vessel at 40–50 °C $(\text{SN})_n$ decomposes into sulphur, nitrogen, and other as yet unidentified compounds. No change is observed in the X-ray diffraction pattern when $(\text{SN})_n$ is exposed to the atmosphere for two weeks, or after exposure for six days to an atmosphere of one mole of dry or moist oxygen. However, slow decomposition takes place when the polymer is added to degassed distilled water.

Polythiazyl consists of an almost planar chain of alternating sulphur and nitrogen atoms (14) with intrachain distances of $\text{S}_a\text{—N}_a$ 1.593(4), $\text{S}_a\text{—N}_b$ 1.628(7), $\text{S}_a\text{—S}_b$ 2.789(2), $\text{N}_a\text{—N}_b$ 2.576(7), and $\text{S}_a\text{—N}_c$ 2.864(5) Å. The bond angles SNS and NSN have values of 119.9(4) and 106.2(2)°, respectively.



An X-ray single-crystal study of S_2N_2 , at –130 °C, shows that the molecule is square planar, the S—N bond lengths having approximately the same value [1.651(1) and 1.657(1) Å] as in $(\text{SN})_n$ the values of the SNS and NSN angles being 90.42(6) and 89.58(6)°, respectively.

2 Group VII

The main areas of importance in the chemistry and properties of the halogens have been the synthesis and structural assignments of polyhalogen species. An X-ray crystallographic structure determination of (theobromine) $_2\text{H}_2\text{I}_8$ shows that the compound is a polyiodide salt containing cationic and anionic layers, the cation consisting of hydrogen-bonded, protonated theobromine species and the anion being I_{16}^{4-} .¹⁹ This polyiodide ion is the largest polyanion to be reported. The shortest distance between adjacent I_{16}^{4-} anions is 3.54 Å, which is of the same order as that observed in the tri-iodide chains in (benzamide) $_2\text{HI}_3$. The large distance between the anions is indicative of there being only a weak interaction and suggests that the I_{16}^{4-} species can be regarded as a discrete polyiodide anion.

The Cl_2^- anion has been identified, by Raman and i.r. studies, from the products of alkali-metal atom matrix reactions with molecular chlorine.²⁰ The yellowish $\text{M}^+ \text{Cl}_2^-$ species produced resonance Raman spectra, and the dissociation energy of the Cl_2^- anion ranges from 1.19 ± 0.06 eV for $\text{Li}^{+35}\text{Cl}_2^-$ to 1.38 ± 0.06 eV for $\text{Cs}^{+35}\text{Cl}_2^-$. The vibrational assignments to the (ν_1) and intraionic (ν_2) symmetric modes of $\text{M}^+ \text{Cl}_2^-$ based on a triangular geometry are given in Table 3.

¹⁹ F. H. Herbstein and M. Kapon, *J.C.S. Chem. Comm.*, 1975, 677.

²⁰ W. F. Howard and L. Andrews, *Inorg. Chem.*, 1975, **14**, 767.

Table 3 *Vibrational assignments for alkali-metal dichlorides*

| Species | ν_1 (wavenumber/cm ⁻¹) | ν_2 (wavenumber/cm ⁻¹) |
|--------------------------------|--|--|
| ⁶ LiCl ₂ | 246 | 552 |
| ⁷ LiCl ₂ | 246 | 518 |
| NaCl ₂ | 225 | (270)* |
| KCl ₂ | 264 | (200)* |
| RbCl ₂ | 260 | (160)* |
| CsCl ₂ | 259 | (140)* |

* Estimated.

Salt-molecule reactions in a matrix have been found to be very effective for the synthesis of polyatomic ionic molecules for spectroscopic study. Reaction of the chloride of sodium, potassium, rubidium, or caesium with hydrogen chloride in an argon matrix results in the formation of the HCl₂⁻ anion in the species M⁺ HCl₂⁻.²¹ A comparison of the ν_3 frequencies and the observed shifts for the deuterium compounds has led to the conclusion that this species is in fact the isolated HCl₂⁻ anion and not the HCl₂ radical as previously assigned. A similar reaction of a Group I metal salt with chlorine results in the formation of the M⁺ Cl₃⁻ species, identified by the ν_3 of the Cl₃⁻ anion.

Argon-matrix reactions of alkali-metal atoms with molecular fluorine have been studied using laser Raman and i.r. spectroscopy.²² The Raman signals appropriate for the ν_1 intraionic (F \leftrightarrow F)⁻ mode in the M⁺ F_a⁻ species, show an alkali-metal shift because of the interaction with the ν_2 intraionic M⁺-F₂⁻ mode. The vibrational assignments for the symmetric modes of the M⁺F₂⁻ species based on a triangular geometry are given in Table 4.

Table 4 *Vibrational assignments for alkali-metal difluorides*

| Species | ν_1 (wavenumber/cm ⁻¹) | ν_2 (wavenumber/cm ⁻¹) |
|-------------------------------|--|--|
| ⁶ LiF ₂ | 452 | 708 |
| ⁷ LiF ₂ | 452 | |
| NaF ₂ | 475 | 454 |
| KF ₂ | 464 | 342 |
| RbF ₂ | 462 | (266)* |
| CsF ₂ | 459 | (248)* |

* Possibly due to (MF)₂.

The HF₂⁻ anion has aroused considerable attention owing to the possibility of a double minimum potential for the hydrogen atom. Structural studies by X-ray analysis of *p*-toluidinium bifluoride show the anion to be linear and symmetric, in contrast to the results from neutron diffraction studies which found the (F...H—F)⁻ ion to be linear but with different H—F bond lengths. However, calculations based on the effect of an external point charge on the bifluoride geometry have been made,²³ and show that both fluorine atoms move towards the positive charge, hence shortening one H—F bond and lengthening the other. A point charge therefore will affect the geometry of the HF₂⁻ anion and hence the asymmetric geometry of the HF₂⁻ anion in *p*-toluidinium bifluoride can be partly explained by its asymmetric crystal field.

²¹ B. S. Ault and L. Andrews, *J. Amer. Chem. Soc.*, 1975, **97**, 3824.²² W. F. Howard and L. Andrews, *Inorg. Chem.*, 1975, **14**, 409.²³ N. S. Ostlund and L. W. Ballenger, *J. Amer. Chem. Soc.*, 1975, **97**, 1237.

The products of the argon-matrix reaction of iodine and an alkali metal have been investigated by Raman spectroscopy.²⁴ The six-membered vibrational progression, beginning near 115 cm^{-1} , decreases in intensity and increases in bandwidth in a regular manner with increasing vibrational quantum number for lithium, sodium, potassium, rubidium, and caesium. The values obtained for the dissociation energies for lithium, sodium, and potassium are 88, 84, and 75 kJ mol^{-1} , respectively.

The chlorine hexafluoride radical has been obtained by γ -radiolysis of sulphur hexafluoride containing 5 mole % of chlorine pentafluoride at -196°C .²⁵ The e.s.r. spectrum has been assigned and ClF_6 has been found to have a large ^{35}Cl coupling of 77.1 mT , which is more than twice the value for ClF_4 . It is concluded that the unpaired electron in ClF_6 must populate the chlorine $3s$ -orbital.

The i.r. spectrum and force field of the hexafluorobromine cation, obtained by the action of excess BrF_6 and a 2 : 1 molar ratio of KrF_2 - AsF_5 , has been recorded.²⁶ The stretching force constant for the $[\text{BrF}_6]^+$ cation has a value of 4.9 mdyn \AA^{-1} which is the highest value observed for any BrF bond. As these bonds are much stronger than in other bromine fluorides, the reactivity of $[\text{BrF}_6]^+$ salts must be due to its high oxidizing power.

The chlorine n.q.r. frequencies have been reported for Ph_4AsCl_3 , Et_4NCl_3 , $\text{Me}_4\text{NBrCl}_2$, and Me_4NlCl_2 .²⁷ In the trichloride ion, the negative charge is divided evenly between the two terminal atoms with the central chlorine atom having a slight positive charge. The negative charge on the chlorine atom increases as the central atom varies from chlorine, through bromine, to iodine. The charge distributions observed are consistent with Rundle delocalized three-centre, four-electron bonds involving s - and p -orbitals and are indicative of little or no d -orbital contribution.

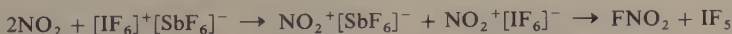
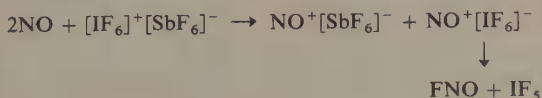
The i.r. and Raman studies on the 1 : 1 complex between iodine heptafluoride and antimony pentafluoride are consistent with the complex having the ionic structure $[\text{IF}_6]^+[\text{SbF}_6]^-$.²⁸ In contrast to most halogenofluorine-metal fluoride complexes, which usually react violently with water, $[\text{IF}_6]^+[\text{SbF}_6]^-$ undergoes a smooth exothermal hydrolysis:



Although $[\text{IF}_6]^+[\text{SbF}_6]^-$ reacts with carbon monoxide,



there is only a slight reaction with methane or sulphur dioxide, and no reaction with carbon dioxide. Both nitric oxide and nitrogen dioxide react to form stable non-volatile complexes:



²⁴ W. F. Howard and L. Andrews, *J. Amer. Chem. Soc.*, 1975, **97**, 2956.

²⁵ K. Nishikida, F. Williams, G. Maniantov, and N. Smyrst, *J. Amer. Chem. Soc.* 1975, **97**, 3526.

²⁶ K. O. Christie and R. D. Wilson, *Inorg. Chem.*, 1975, **14**, 694.

²⁷ E. F. Riedel and R. D. Willet, *J. Amer. Chem. Soc.*, 1975, **97**, 701.

²⁸ F. A. Hohorst, L. Stein, and E. Gebert, *Inorg. Chem.*, 1975, **14**, 2233.

However, the most significant property of $[\text{IF}_6]^+[\text{SbF}_6]^-$ is its reaction, at ambient temperature, with radon, forming an unidentified non-volatile Rn compound. This has important implications for the analysis of radon in air and also for gas purification. However, although the oxidation potential of $[\text{IF}_6]^+$ is high enough to oxidize Rn, no reaction with Xe was observed.

3 Group VIII

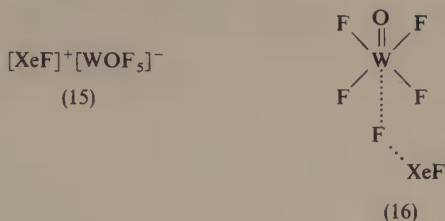
Xenon difluoride forms adducts with some metal pentafluorides and these adducts have been assigned ionic structures. However, recent spectral evidence suggests that in many of these compounds there is considerable covalent bonding, involving fluoride bridges between the cation and the anion. For example, from the reaction of xenon difluoride with the pentafluorides of antimony, tantalum, and niobium three types of adduct have been identified having the $\text{XeF}_2:\text{MF}_5$ mole ratios 2:1, 1:1, and 1:2. On the basis of Raman and X-ray crystallographic studies the adducts have been formulated as $[\text{Xe}_2\text{F}_3]^+[\text{MF}_6]^-$, $[\text{XeF}]^+[\text{MF}_6]^-$, and $[\text{XeF}]^+[\text{M}_2\text{F}_{11}]^-$. However, recent Raman spectroscopic studies strongly suggest some covalent bonding in that the spectra of the $\text{XeF}_2:\text{MF}_5$ adducts can be more satisfactorily assigned on the basis of C_{4v} symmetry for the hexafluoro-anion than O_h symmetry. The results are consistent with a significant lowering of the symmetry of the octahedral anion by fluoride bridging to the $[\text{XeF}]^+$ cation. As the $\nu(\text{XeF})$ is totally symmetric, the splitting of $\nu(\text{XeF})$ in many adducts has been attributed to factor-group splitting. However, the mean value of the stretching frequency associated with $\nu(\text{XeF}^+)$ for the $\text{XeF}_2, 2\text{MF}_5$ and $\text{XeF}_2:\text{MF}_5$ series of adducts decreases in the order $\text{SbF}_5 > \text{TaF}_5 > \text{NbF}_5$. These results are consistent with the suggestion that the XeF bond length in $[\text{XeF}]^+$ is progressively increasing. A comparison of the peaks which have been assigned to $\nu(\text{Xe}\cdots\text{F})$ shows a progressive increase in value of the mean frequency, which is indicative of an increasing strength of the bridging bond.²⁹

Previously, the spectrum of $\text{XeF}_2:\text{SbF}_5$ was assigned on the assumption of O_h symmetry for the anion. However, definitive assignment for the anion modes has proved difficult since in the case of the Sb and Ta adducts more than six anion modes were observed. If the adducts which were previously formulated as the ionic species $[\text{XeF}]^+[\text{MF}_6]^-$ are reformulated as having a fluoride-bridged structure of the type $\text{XeF}^+\text{FMF}_5^-$, in which the anion can be regarded as distorted from O_h to C_{4v} symmetry, then the observed spectral bands can be assigned more satisfactorily. The bands in all the spectra in the region $450\text{--}490\text{ cm}^{-1}$ are not easily assignable to vibrations of octahedral $[\text{MF}_6]^-$ anions and are better assigned to additional $\nu(\text{M}\cdots\text{F})$.

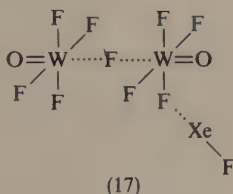
In conclusion, the i.r. and Raman spectra of the adducts $2\text{XeF}_2:\text{MF}_5$ ($\text{M} = \text{Sb}$ or Ta), $\text{XeF}_2:\text{MF}_5$, and $\text{XeF}_2, 2\text{MF}_5$ ($\text{M} = \text{Sb}$, Ta , or Nb) have been measured, and although the spectra have been interpreted in terms of an ionic formulation involving $[\text{XeF}]^+$ and $[\text{Xe}_2\text{F}_3]^+$ the results indicate an increasing covalent character in the series $\text{XeF}_2:\text{SbF}_5 < \text{XeF}_2:\text{TaF}_5 < \text{XeF}_2:\text{NbF}_5 < \text{XeF}_2, 2\text{TaF}_5 < \text{XeF}_2, 2\text{NbF}_5$, and $2\text{XeF}_2:\text{SbF}_5 < 2\text{XeF}_2:\text{TaF}_5$.

²⁹ B. Frlac and J. H. Holloway, *J.C.S. Dalton*, 1975, 535.

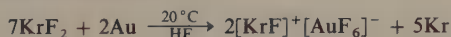
Further evidence for the covalent nature comes from a Raman and ^{19}F n.m.r. study of adducts of xenon difluoride with WOF_4 .³⁰ Stoichiometric amounts of XeF_2 and WOF_4 react in HF at room temperature and in the melts at 30–75 °C to give stable crystalline solids at room temperature. Two possible structures are the ionic form (15) and the partially covalent form (16). The low-temperature ^{19}F n.m.r. spectra of



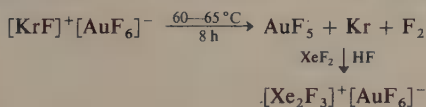
solutions in BrF_5 and SO_2ClF support the covalent structure,³⁰ which is further supported by bands in the Raman spectrum which can be assigned to a fluoride-bridged structure. In $\text{XeF}_2, \text{WOF}_4$ the structural unit has approximately C_s symmetry. The terminal XeF bond length (1.89 Å) is shorter than that of XeF_2 (2.00 Å) while the $\text{Xe}\cdots\text{F}$ bridge bond length (2.04 Å) is longer than the XeF bonds in XeF_2 . The $\text{W}\cdots\text{F}\cdots\text{Xe}$ bridge angle is 147°. The Raman spectrum of $\text{XeF}_2, 2\text{WOF}_4$ is also consistent with a bridged structure (17). However, the ^{19}F n.m.r. spectrum of a SO_2ClF solution of $\text{XeF}_2, 2\text{WOF}_4$ is complex and, in addition to lines associated with the fluoride-bridged structures, lines were also observed consistent with an oxo-bridged structure.



Krypton difluoride is a very powerful oxidative fluorinating agent and has been used to synthesize gold(v) species:³¹



Raman studies at –80 °C under a layer of HF are consistent with a formulation in which the $[\text{KrF}]^+$ cation is fluoride-bridged to a $[\text{AuF}_6]^-$ anion with lines assignable to a C_{4v} symmetry for $[\text{AuF}_6]^-$. $[\text{KrF}]^+[\text{AuF}_6]^-$ on pyrolysis gives AuF_5 , a powerful oxidative fluorinating agent, which react with an excess of XeF_2 :



³⁰ J. H. Holloway, G. J. Schrobilgen, and P. Taylor, *J.C.S. Chem. Comm.*, 1975, 40.

³¹ J. H. Holloway and G. J. Schrobilgen, *J.C.S. Chem. Comm.*, 1975, 623.

Raman and ^{19}F n.m.r. studies on the products of the reaction of $[\text{KrF}]^+$ salts with excess of XeOF_4 show them to be O_2^+ and $[\text{XeOF}_4\text{XeF}_5]^+$ salts and not XeOF_5 as previously reported.

Relativistic quantum mechanics applied to radon (or element 118) fluoride structures indicates that ionic crystalline forms are probably more stable for the fluorides of these elements, in contrast to the molecular forms of xenon fluorides.³² An ionic crystalline form of RnF would be expected to be non-volatile, as found, and show the observed migration of Rn as a cation upon electrolysis.

³² K. S. Pitzer, *J.C.S. Chem. Comm.*, 1975, 760.

7 Transition-metal Chemistry

By J. R. DILWORTH, G. J. LEIGH, and R. L. RICHARDS

ARC Unit of Nitrogen Fixation, University of Sussex, Falmer, Sussex, BN1 9QJ

1 Groups IV and V: Titanium, Zirconium, and Hafnium; Vanadium, Niobium, and Tantalum

In contrast to the explosion of organometallic and complex chemistry which has been concentrated at the right-hand end of the Transition Series, the left-hand end has been somewhat neglected, and much of its inorganic chemistry has proceeded along well-tried classical paths involving such areas as phase-studies and formation of polymeric oxo-species in solution. Of late, however, there has been greater emphasis on extending to Groups IV and V the techniques and ideas established with, for example, the platinum metals, and consequently new insights are being obtained.

The elements of Groups IV and V are electron-deficient in their complexes as judged by the 18-electron rule. Their chemistry, which shows a preference for higher rather than lower oxidation states, often belies this. Co-ordination number 5 (as in $[\text{TiCl}_5]^-$ and $[\text{TiBr}_5]^-$) is not usual for titanium(IV), but has been observed in a dichloromethane solution containing TiCl_4 or TiBr_4 and the appropriate halide.¹ In the solid state these ions are dimerized through halogen bridges. Co-ordination number 6 is of course, common, but is not without surprises. The anion in $[\text{AsPh}_4][\text{Ta}(\text{benzenedithiolate})_3]$ exhibits trigonal-prismatic co-ordination,² but whereas the niobium analogue is regular, one of the dithiolates in the tantalum complex is twisted about the two-fold axis by *ca.* 12°, and the other two are bent about the S—S axis. No explanation is forthcoming.

Co-ordination number 7 has been reported³ in complexes such as $[\text{TaCl}_3\text{L}_2]$ ($\text{L} = \text{NN}'\text{-dicyclohexylacetamidinate}$), which form distorted pentagonal bipyramids with halides in the axial position. However, co-ordination number 8 is apparently much more common, but several stereochemistries appear possible.

The complex $\text{K}_4[\text{Nb}(\text{CN})_8]\cdot 2\text{H}_2\text{O}$ is apparently isomorphous with its molybdenum analogue, and thus $[\text{Nb}(\text{CN})_8]^{4-}$ is probably dodecahedral. This is confirmed by the e.s.r. spectrum, which also is interpreted as showing that in solution in glycerol the ion takes on an antiprismatic configuration.⁴ The antiprismatic structure has now been identified for the first time in a solid of the type $[\text{M}(\text{LL}')_4]$ for $\text{M} = \text{Nb}$ and $\text{LL}' = 2,2,6,6\text{-tetramethylheptane-3,5-dionate}$.⁵ Another variant has been recognized in the complex $[\{\text{Nb}(\text{C}_7\text{H}_5\text{O}_2)_4\}_2\text{O}(\text{HCl})_3]\cdot \text{MeCN}$.⁶ The tropolonate ligand is

¹ C. S. Creaser and J. A. Creighton, *J.C.S. Dalton*, 1975, 1402.

² J. L. Martin and J. Takats, *Inorg. Chem.*, 1975, **14**, 1358.

³ M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1975, 2611.

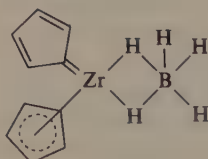
⁴ P. M. Kiernan and W. P. Griffith, *J.C.S. Dalton*, 1975, 2489.

⁵ T. J. Pinnavaia, B. L. Barnett, G. Podolsky, and A. Tulinsky, *J. Amer. Chem. Soc.*, 1975, **97**, 2712.

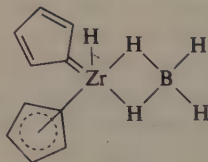
found to have a very short bite [2.43(2) Å, compared with a previous shortest bite of 2.490(6) Å]. This may be associated with the very short interligand distances observed, but the 'NbO₈' nucleus is best described as 'an irregular bicapped trigonal prism'.⁶ It is likely, however, that the dodecahedral structure, as evidenced by [NbX₄(diarsine)₂] (X = Cl or Br)⁷ and [MCl₄(diarsine)₂]⁺,⁸ is the most common.

It is evident that the various structures available for eight co-ordination are not widely separated in energy, so that non-rigidity is common. The complex [Zr(acac)₂(NO₃)₂] (acac = acetylacetonate) exhibits a distorted dodecahedral co-ordination in the solid state,⁹ and the reasons for the particular stereoisomer which is observed have been discussed. In solution the number of co-ordinating groups does not change, but the complex is stereochemically non-rigid on the n.m.r. timescale down to -130 °C, with a coalescence temperature of -144 °C. The complex ion [Ta(S₂CNMe₂)₄]⁺ is also dodecahedral in the solid state.¹⁰ However, in solution the coalescence temperature is -62 °C, whereas the isoelectric [M(S₂CNEt₂)₄] (M = Ti, Zr, or Nb) is non-rigid down to at least -140 °C. The reasons for these differences are not evident.

There have also been developments in classes of compounds which have been known for some time. Thus tetrahedral titanium has been resolved for the first time in, e.g. [(π-C₅H₄CHMePh)(π-C₅H₅)PhTiCl]¹¹ and [(π-C₅H₄CMe₂Ph)(π-C₅H₅)TiCl(OPh)]¹² (see also Chapter 8, p. 192, Scheme 5). The complexes [M(BH₄)₄] (M = Zr or Hf) can be considered as having the metal in a co-ordination number of 12 since each borohydride ion is bonded to the metal *via* a triple-hydrogen bridge. It was suggested some time ago that the borohydride group in these systems can be regarded as a three-electron donor (*cf.* allyl) and thus the compounds are 16-electron species. However, a simple group-theoretical argument has been held to show that the borohydride group is, in fact, a 3.5-electron donor.¹³ It is not easy to envisage what this means, particularly as there are no geometrical consequences (*cf.* NO) of this assignment. However, the arguments are based upon B—H bonding electrons being involved in linkage to the metal, and no others. A Raman and i.r. study of [Hf(BH₄)₄] and [Hf(BD₄)₄] suggests that these molecules contain a significant amount of direct Hf—B bonding.¹⁴ This alone casts doubt on the concept of a ligand donating specific numbers of electrons to an acceptor.



(1)



(2)

⁶ A. R. Davis and F. B. Einstein, *Inorg. Chem.*, 1975, **14**, 3030.

⁷ D. L. Kepert and K. R. Trigwell, *J.C.S. Dalton*, 1975, 1903.

⁸ J. C. Dewan, D. L. Kepert, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1975, 2031.

⁹ V. W. Day and R. C. Fay, *J. Amer. Chem. Soc.*, 1975, **97**, 5136.

¹⁰ R. C. Fay, D. F. Lewis, and J. R. Weir, *J. Amer. Chem. Soc.*, 1975, **97**, 7179.

¹¹ C. Moise, J. C. Leblanc, and J. Tirouflet, *J. Amer. Chem. Soc.*, 1975, **97**, 6272.

¹² A. Dormond, J. Tirouflet, and F. Le Moigne, *J. Organometallic Chem.*, 1975, **101**, 71.

¹³ A. Davison and S. S. Wreford, *Inorg. Chem.*, 1975, **14**, 703.

¹⁴ T. A. Keiderling, W. T. Wozniak, R. S. Gay, D. Jarkowitz, E. R. Bernstein, S. J. Lippard, and T. G. Spiro, *Inorg. Chem.*, 1975, **14**, 576.

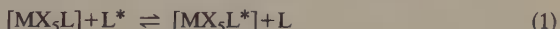
Complexes such as $[(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2]$ contain double-hydrogen bridges. However, there is a rapid exchange of hydrogens between the B—H bonds and the C_5H_5 rings. Methylene intermediates such as (1) and (2) have been proposed to explain this exchange.¹⁵ It is likely that this kind of H-transfer from the ring is common in $(\pi\text{-cyclopentadienyl})$ -complexes of Groups IV and V.

An X-ray photoelectron spectroscopic study of volatile vanadium compounds has been reported.^{16a} It is calculated that even in VF_5 the positive charge on the vanadium is not much greater than one unit and in VCl_4 it is considerably less. In $[\text{V}(\text{CO})_6]$ the carbon monoxide is a net electron acceptor. All this accords with a growing amount of data gathered from other elements. A study of some complexes of pyridine-2,6-dicarboxylic acid¹⁷ gave no indication of the formal oxidation state of the vanadium. This also accords with more general experience. A u.v. photoelectron study of $[\text{M}(\text{NMe}_2)_4]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}$, or a typical element of Group IV), as well as of $[\text{W}(\text{NMe}_2)_6]$, has shown that except for $\text{M} = \text{V}$, the first band(s) arises from MO's which are linear combinations of nitrogen lone-pair AO's.^{16b}

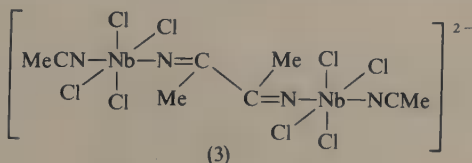
Studies¹⁸ of vanadium tetraphenylporphyrin derivatives have shown that substituents in the phenyl ring have little effect on equilibrium constants or e.s.r. parameters. This is in contrast to the nickel analogues, and the reason is not clear.

A detailed preparative investigation of vanadium nitrosyls has been reported.¹⁹ This is not a trivial matter, because NO tends to attack both metal and certain ligands (such as phosphines) yielding oxo-complexes and ligand oxides. Vanadium(IV) chloride reacts with NO in carbon tetrachloride at 20°C to yield $[\text{V}(\text{NO})_3\text{Cl}_2]$, possibly via $[\text{V}(\text{NO})\text{Cl}_4]$. The tris(nitrosyl) reacts with hard nitrogen- and oxygen-bases, L, to yield $[\text{V}(\text{NO})\text{Cl}_2\text{L}_n]$, which have $\nu(\text{NO})$ at ca. 1650 cm^{-1} . Triphenylphosphine oxide in benzene yields $[\text{V}(\text{NO})(\text{PPh}_3\text{O})_4\text{Cl}]\text{Cl}$, and triphenylphosphine in chloroform produces $[\text{VOCl}_2(\text{PPh}_3\text{O})_2]$. Bis(diphenylphosphino)ethane does not react with $[\text{V}(\text{NO})_3\text{Cl}_2]$ because, it is suggested, it is too soft.

Groups IV and V show a distinct preference for harder rather than softer ligands, and this can even affect reaction mechanisms. Thus, in the equilibrium (1) ($\text{M} = \text{Nb}$ or Ta ; $\text{X} = \text{F}, \text{Cl}$, or Br) it is found that the mechanism is primarily a dissociative one for $\text{L} = \text{Me}_2\text{O}$ or Et_2O , and associative for $\text{L} = \text{Me}_2\text{S}$, Me_2Se , or Me_2Te .²⁰



The compounds MCl_4 ($\text{M} = \text{Ti}$ or V) and MCl_5 ($\text{M} = \text{Nb}$ or Ta) form simple adducts with $\text{C}_6\text{H}_5\text{CN}$. With acetonitrile, however, NbCl_4 and TaCl_4 yield, amongst other



¹⁵ T. J. Marks and J. R. Kolb, *J. Amer. Chem. Soc.*, 1975, **97**, 3397.

¹⁶ (a) R. R. Rietz, T. F. Schaaf, and W. L. Jolly, *Inorg. Chem.*, 1975, **14**, 2818; (b) S. G. Gibbins, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J.C.S. Dalton*, 1975, 72.

¹⁷ D. L. Hoof and R. A. Walton, *Inorg. Chim. Acta*, 1975, **12**, 71.

¹⁸ F. A. Walker, E. Hui, and J. M. Walker, *J. Amer. Chem. Soc.*, 1975, **97**, 2390.

¹⁹ W. Beck, H. G. Fick, K. Lottes, and K. H. Schmidtner, *Z. anorg. Chem.*, 1975, **416**, 97.

²⁰ R. Good and E. Merbach, *Inorg. Chem.*, 1975, **97**, 1030.

compounds, dinuclear complexes (3).²² This is presumably a consequence of the strong Lewis acid character of the halides. Methyl isocyanide has been found to insert into the metal-chlorine bonds of MCl_3 ($\text{M} = \text{V}$ or Ti) and MCl_4 ($\text{M} = \text{Ti}$, Zr , or Hf) to yield derivatives containing the $-\text{CCl}=\text{NR}$ grouping.²³ Titanium(IV) chloride behaves as a Lewis acid with the base $[\text{Pt}(\text{PPh}_3)_4]$, which forms $[(\text{TiCl}_4)_2\{\text{TiCl}_4(\text{PPh}_3)_3\}\text{Pt}]$, and then this reacts further with triphenylphosphine to yield $[(\text{TiCl}_4, \text{PPh}_3)_2\text{Pt}]$. The adduct $[(\text{TiCl}_4, \text{PPh}_3)_2\text{Pt}]$ was also described.²⁴ Titanium(IV) nitrate is a strong oxidizing agent which can nitrate aromatics at room temperature. Its electronic structure has been correlated with its observed electron deficiency.²⁵

Pentakis(*NN*-dimethylcarbamato)niobium(v) undergoes stepwise and facile exchange with gaseous carbon dioxide.²⁶ The complex itself is eight-co-ordinate, with two unidentate and three bidentate dithiocarbamates, and it is also formed rapidly from $[\text{Nb}(\text{NMe}_2)_5]$ and CO_2 . The CO_2 exchange is believed to be due to the extrusion of CO_2 to form a tetrakis(carbamato)amido-complex which has been detected in solution and which reacts with CO_2 to reform the pentakis(carbamato)-complex.

The mechanisms of rearrangement of chelate complexes have received attention during the past year. Complexes $[\text{Ti}(\text{dik})_2(\text{NCO})_2]$ and $[\text{Ti}(\text{dik})_2(\text{NCS})_2]$ ($\text{dik} = \text{RCOCHCOR}$; $\text{R} = \text{Me}$ or Bu^t) have been described in considerable detail; they invariably have a *cis*-configuration.²⁷ N.m.r. studies indicate that the alkyl groups of the diketone are exchanging by a process which does not involve rupture of any of the metal-ligand bonds. A similar exchange has been reported to occur in *cis*- $[\text{Ti}(\text{acetylacetonate})_2(\text{OPh})_2]$.²⁸ This is consistent with a body of older data. It has now been pointed out^{29a} that because the rates for methyl interchange of the acetylacetonate groups of $[\text{Ti}(\text{acetylacetonate})_2(\text{OCHMe}_2)_2]$ are the same as those for the methyl interchange of the isopropoxy-groups, then the mechanism of interchange must involve inversion of the helicity of the chelate rings. This inference concerning mechanism is confirmed by another n.m.r. study^{29b} which also agrees with earlier work in suggesting that bond rupture should not be involved in the interchanges.

The structures of some compounds have also been determined by less usual methods. Thus comparison of the diffusion coefficients of NbCl_5 and NbCl_4 and of ZrCl_4 and NbCl_5 leads to the conclusion that NbCl_4 is a dimer in the gas phase.³⁰ An n.q.r. study of MX_5 ($\text{M} = \text{Nb}$ or Ta ; $\text{X} = \text{F}$, Cl , or Br) shows that NbF_5 is a tetramer.³¹

²¹ J. D. Wilkins, *J. Organometallic Chem.*, 1975, **92**, 27.

²² P. A. Finn, M. S. King, P. A. Kilty, and R. E. McCarley, *J. Amer. Chem. Soc.*, 1975, **97**, 220.

²³ B. Crociani, M. Nicolini, and R. L. Richards, *J. Organometallic Chem.*, 1975, **101**, Cl.

²⁴ J. F. Plummer and E. P. Schram, *Inorg. Chem.*, 1975, **14**, 1505.

²⁵ C. D. Garner, I. H. Hillier, and M. F. Guest, *J.C.S. Dalton*, 1975, 1934.

²⁶ M. H. Chisholm and M. Extine, *J. Amer. Chem. Soc.*, 1975, **97**, 1623.

²⁷ A. F. Lindmark and R. C. Fay, *Inorg. Chem.*, 1975, **14**, 282.

²⁸ J. F. Harrod and K. R. Taylor, *Inorg. Chem.*, 1975, **14**, 1541.

²⁹ (a) P. Finocchiaro, *J. Amer. Chem. Soc.*, 1975, **97**, 4443; (b) N. Baggett, D. S. P. Poolton, and W. B. Johnson, *J.C.S. Chem. Comm.*, 1975, 239.

³⁰ A. D. Westland, *Z. anorg. Chem.*, 1975, **414**, 284.

³¹ G. K. Sernin, S. L. Kuznetsov, I. M. Alimov, T. L. Khotsianova, E. V. Bryukhova, L. A. Nisselson, and K. Tretyakova, *Inorg. Chim. Acta*, 1975, **13**, 181.

An electron diffraction study of VOCl_3 shows it to be roughly tetrahedral.³² The penta(thiocyanates) of niobium and tantalum are dimers.³³

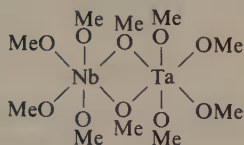
The structures of metal alkoxides have long been intriguing, and a considerable amount of work has been carried out on new alkoxides. Thus, the isopropoxides $[\text{MM}'(\text{OPr}^i)_8]$ and $[\text{MM}'_2(\text{OPr}^i)_{11}]$ ($\text{M} = \text{Nb}$ or Ta ; $\text{M}' = \text{Ga}$ or Al) have been characterized and the structures (4) and (5) proposed.³⁴ A mixed alkoxide containing two different transition elements has been reported for the first time: it is $[\text{NbTa}(\text{OMe})_{10}]$ (6).



(4)



(5)



(6)

The potentially novel allyloxides of titanium, niobium, and tantalum have been reported, but they appear to be normal alkoxide dimers.³⁶ Alkoxide dimers such as $[\text{Nb}_2(\text{OMe})_{10}]$ form adducts $[\text{Nb}(\text{OMe})_5\text{L}]$ with a variety of bases L, where L can be a primary or secondary amine, ammonia, an amine oxide, or a phosphine oxide.³⁷ Compounds L such as tertiary amines, ethers, sulphides, phosphates, nitriles, or sulfoxides do not form adducts, and the overall pattern of behaviour of the various ligands L does not correlate with hard-soft classifications or ideas concerning π -bonding. Steric factors may be overriding. The tantalum complexes have higher formation constants than their niobium analogues.³⁷

There has been considerable activity in the classical areas of oxo-derivatives and oxo-polyanions. Vanadium bis(metaphosphate) and tris(metaphosphate) have been prepared as crystals and their structures inferred.³⁸ The former probably contains vanadium(IV) co-ordinated by oxygen atoms in a distorted octahedron aligned along a crystal axis and with the chains of octahedra linked by metaphosphate chains. The tris(metaphosphate) also has octahedrally co-ordinated vanadium. New polyvanadates, for example $\text{Ba}_2\text{VSi}_2\text{O}_8$, $\text{Ba}_2\text{V}_2\text{O}_7$, $\text{Ba}_6\text{V}_6\text{O}_{14}$, and $\text{Sr}_6\text{V}_6\text{O}_{11}$ have been characterized.³⁹ The preparation and thermal decomposition of $\text{Nb}_3\text{O}_7\text{Cl}$ have been described.⁴⁰ The constitution and interconversions of the polyvanadates have received considerable attention. The nature of decavanadates in the solid state and in acidic and basic conditions has been studied. The i.r. spectra of solid state and acidic solutions show no sign of hexavanadate formation and are consistent with the presence of $[\text{V}_{10}\text{O}_{28}]^{6-}$ only, or of some protonated species immediately derivable from it.⁴¹ The n.m.r. data can also be rationalized on this basis. Base titration and

³² T. Karakida and K. Kuchitsu, *Inorg. Chimica Acta*, 1975, **13**, 113.

³³ H. Böhlund and E. Harke, *Z. anorg. Chem.*, 1975, **413**, 102.

³⁴ S. Govil, P. N. Kapoor, and R. C. Mehrotra, *Inorg. Chim. Acta*, 1975, **15**, 43.

³⁵ L. G. Hubert-Pfalzgraf and J. G. Riess, *Inorg. Chem.*, 1975, **14**, 2854.

³⁶ P. N. Kapoor, S. K. Mehrotra, R. B. King, and K. C. Nainan, *Inorg. Chim. Acta*, 1975, **12**, 273.

³⁷ L. G. Hubert-Pfalzgraf, *Inorg. Chim. Acta*, 1975, **12**, 229.

³⁸ B. C. Tofield, G. R. Crane, G. A. Pasteur, and R. C. Sherwood, *J.C.S. Dalton*, 1975, 1806.

³⁹ A. Feltz, S. Schmalfuss, H. Langbein, and M. Tietz, *Z. anorg. Chem.*, 1975, **417**, 125.

⁴⁰ H. Kodama and M. Goto, *Z. anorg. Chem.*, 1975, **415**, 185.

⁴¹ F. Corigliani and S. Di Pasquale, *Inorg. Chim. Acta*, 1975, **12**, 99.

extraction into non-aqueous solution allowed⁴² the identification of a series of protonated decavanadates $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$, $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$, and $[\text{HV}_{10}\text{O}_{28}]^{5-}$, as well as $[\text{V}_{10}\text{O}_{28}]^{6-}$. In basic solution decavanadate decomposes to form $[\text{VO}_4]^{3-}$, and this decomposition has been shown to proceed *via* both base-dependent and base-independent paths.⁴³ The base-dependent path involves a reactive alkali-metal cation decavanadate species. Basic solutions of $[\text{VO}]^{2+}$ have been studied by a variety of techniques.⁴⁴ The ion $[\text{VO}(\text{OH})_3]^-$ of uncertain degree of aquation is predominant, and higher oligomers are unimportant. In fact, the aquated ion is likely to be $[\text{VO}(\text{OH})_3(\text{H}_2\text{O})_2]^-$ on the basis of optical and e.s.r. spectra, and related to $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ by simple protonation.

2 Group VI: Chromium, Molybdenum, and Tungsten

Complexes with Metal-Metal Bonds.—A recurrent theme in the chemistry of this triad has been the chemistry of derivatives with metal-metal multiple bonds. A comprehensive review of the subject to the end of 1974 has been published.⁴⁵

Calculations by the SCF scattered-wave $X\alpha$ method for $[\text{Mo}_2\text{Cl}_8]^{4-}$ ion⁴⁶ provide striking confirmation for Cotton's original proposals on the nature of the metal-metal quadruple bond. A set of Mo—Mo bonding orbitals, of predominantly metal d -character, in the order (of increasing energy) σ , π , δ were found, as required for the σ , π , and δ overlap model. An empty δ^* orbital lies just above the δ orbital, and the peak observed at *ca.* 19 000 cm^{-1} in the electronic spectrum of $[\text{Mo}_2\text{Cl}_8]^{4-}$ ions can now be assigned to a dipole-allowed $\delta \rightarrow \delta^*$ transition. Improved resonance Raman spectra of $[\text{Mo}_2\text{Cl}_8]^{4-}$ ions with a range of counter-ions have been reported⁴⁷ together with their electronic spectra. The technique involves irradiation with an exciting frequency within the contour of an allowed electronic transition and causes enormous enhancement of bands due to the fundamental metal-metal stretching vibration ν_1 at 346 cm^{-1} . Overtones of up to 11 ν_1 are observed for the dicaesium salt.

Solution of $\text{K}_4[\text{Mo}_2\text{Cl}_8]$ in 0.1M- HSO_3CF_3 and addition of K_2SO_4 gives pink $\text{K}_4[\text{Mo}_2(\text{SO}_4)_4] \cdot 2\text{H}_2\text{O}$, which on attempted recrystallization also forms lavender crystals of $\text{K}_3[\text{Mo}_2(\text{SO}_4)_4] \cdot 3.5\text{H}_2\text{O}$.⁴⁸ Both complexes have the same structural skeleton (7) with Mo—Mo bond lengths of 2.111(1) and 2.164(2) Å, respectively, and are related by an $E_{1/2}$ redox potential of 0.22 V *vs.* SCE. The complex $[\text{Mo}_2\{\text{PhC}(\text{NPh})_2\}_4]$ prepared by heating $[\text{Mo}(\text{CO})_6]$ with NN' -diphenylbenzamidine, has a structure analogous to the acetates $[\text{Mo}_2(\text{O}_2\text{CR})_4]$ with the amidine groups bridging the two molybdenums.⁴⁹ Attempts to prepare the chromium and tungsten analogues gave uncharacterized products appearing to contain arene-tricarbonyl moieties.

⁴² F. Corigliani and S. Di Pasquale, *Inorg. Chim. Acta*, 1975, **12**, 102.

⁴³ D. M. Druskovich and D. L. Kepert, *J. C. S. Dalton*, 1975, 947.

⁴⁴ M. M. Iannuzzi and P. H. Rieger, *Inorg. Chem.*, 1975, **14**, 2895.

⁴⁵ F. A. Cotton, *Chem. Soc. Rev.*, 1975, **4**, 27.

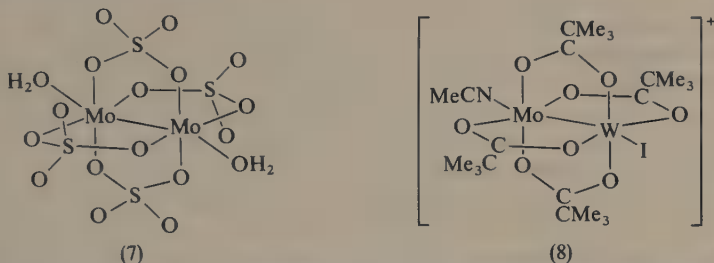
⁴⁶ J. G. Norman and H. J. Kolari, *J. Amer. Chem. Soc.*, 1975, **97**, 33.

⁴⁷ R. J. H. Clark and M. L. Franks, *J. Amer. Chem. Soc.*, 1975, **97**, 2691.

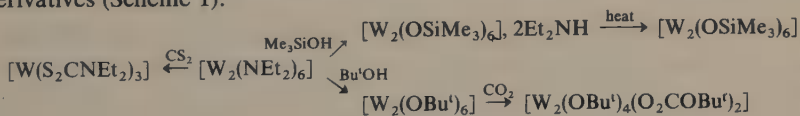
⁴⁸ A. R. Bowen and H. Taube, *Inorg. Chem.*, 1974, **13**, 2245; F. A. Cotton, B. A. Frenz, E. Pedersen, and T. R. Webb, *Inorg. Chem.*, 1975, **14**, 391.

⁴⁹ F. A. Cotton, T. Inglis, M. Kilner, and T. R. Webb, *Inorg. Chem.*, 1975, **14**, 2023.

Following last year's report⁵⁰ of the preparation of $[\text{CrMo}(\text{O}_2\text{CMe})_4]$, $[\text{MoW}(\text{O}_2\text{CBu}^t)_4\text{I}]^+(8)$ has been prepared by iodination of benzene solutions of an inseparable mixture of $[\text{Mo}_2(\text{O}_2\text{CBu}^t)_4]$ and $[\text{MoW}(\text{O}_2\text{CBu}^t)_4]$.⁵¹ A crystal structure of an acetonitrile solvate of cation (8) showed that the iodine is bonded exclusively to the tungsten. Reduction with zinc in acetonitrile gave pure samples of the uncharged derivative $[\text{MoW}(\text{O}_2\text{CBu}^t)_4]$.



The reaction between $[\text{WCl}_4(\text{OEt})_2]$ and three equivalents of LiNMe_2 gives an inseparable 1:2 mixture of $[\text{W}(\text{NMe}_2)_6]$ and dimeric $[\text{W}_2(\text{NMe}_2)_6]$.⁵² An X-ray crystal structure of this mixture confirmed the presence of a triple bond between the tungstens of the dimer with an W—W bond-length of 2.294 Å. The structure and preparation of the molybdenum analogue from MoCl_3 and LiNMe_2 were reported during 1974.⁵³ Use of the sterically more demanding LiNEt_2 favours the formation of dimer relative to monomer and permits preparation of pure $[\text{W}_2(\text{NEt}_2)_6]$,⁵⁴ which serves as a useful starting point for the synthesis of a range of metal-metal bonded derivatives (Scheme 1).



Scheme 1

Two groups of workers^{55,56} have studied the interesting equilibrium between a formally triple and a formally single metal-metal bond (see Chapter 8, p. 196). A surprising feature of the X-ray crystal structure of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ is the near linearity of the $\text{Cp}-\text{Mo}-\text{Mo}-\text{Cp}$ system; the complexes $[\text{Cp}_2\text{M}_2(\text{CO})_6]$ ($\text{M} = \text{Cr}$ or Mo) have pronounced $\text{M}-\text{M}-\text{Cp}$ angles.⁵⁷

Nitrogen Fixation and other Reactions of Biological Significance.— Although the role of molybdenum in biological systems is still largely unknown, there is great current interest in reactions catalysed by molybdoenzymes, particularly nitrogen

⁵⁰ C. D. Garner and R. G. Senior, *J.C.S. Chem. Comm.*, 1974, 586.

⁵¹ V. Katoric, J. L. Templeton, R. J. Hexmeier, and R. E. McCarley, *J. Amer. Chem. Soc.*, 1975, **97**, 5300.

⁵² F. A. Cotton, B. R. Stults, J. M. Troup, M. H. Chisholm, and M. Extine, *J. Amer. Chem. Soc.*, 1975, **97**, 1242.

⁵³ F. A. Cotton, B. A. Frenz, L. Shive, M. H. Chisholm, and W. Reichert, *J.C.S. Chem. Comm.*, 1974, 480.

⁵⁴ M. H. Chisholm and M. Extine, *J. Amer. Chem. Soc.*, 1975, **97**, 5625.

⁵⁵ D. S. Ginley and M. S. Wrighton, *J. Amer. Chem. Soc.*, 1975, **97**, 3535.

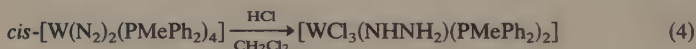
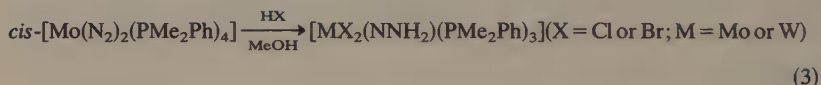
⁵⁶ R. J. Klinger, W. Butler, and M. D. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 3534.

⁵⁷ R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1086; *J. Amer. Chem. Soc.*, 1974, **96**, 749.

fixation. This last subject has been exhaustively reviewed in recent years,⁵⁸ and coverage is here restricted to the 1975 literature.

A significant advance in abiological nitrogen fixation has been the reports^{59,60} of the formation of ammonia from dinitrogen terminally co-ordinated to molybdenum or tungsten. The complex *trans*-[Mo(N₂)₂(dpe)₂] (dpe = Ph₂PCH₂CH₂PPh₂) undergoes up to 37% conversion of one dinitrogen ligand into ammonia when treated with HBr in *N*-methylpyrrolidone (NMP).⁵⁹ It was proposed that [MoBr₂(NNH₂)(dpe)₂] is formed initially and then converted into a nitride *via* a dinuclear Mo—N—N—Mo system. However, protonation of the nitride complexes [MoNX(dpe)₂] gives the nitrene complexes [MoX₂(NH)(dpe)₂] and no ammonia,⁶¹ and it seems possible that the temperatures required to remove the NMP cause partial replacement of the diphosphines by solvent, and degradation of the NNH₂ derivative to ammonia.

Treatment of the complexes *cis*-[M(N₂)₂(PMe₂Ph)₄] (M = Mo or W) with sulphuric acid in methanol gives *ca.* 36% conversion of one dinitrogen ligand into ammonia for M = Mo and up to 90% conversion for M = W.^{60,62} In each case *ca.* 1 mole of dinitrogen is evolved. Although no intermediates could be isolated, the use of other acids and tertiary phosphines permits the isolation of intermediates containing NNH₂ and NHNH₂ groups bound to the metal [equations (3) and (4)].⁶³ However, the mechanism by which these intermediates produce NH₃ is not yet clear. Since base treatment of [MX₂(NNH₂)(PMe₂Ph)₃] gives 1.6 moles of NH₃ for M = W and only half as much for M = Mo, there may well be different mechanisms operative for the two metals. These results clearly suggest that the active site of nitrogenase could comprise a single molybdenum binding site for dinitrogen which is then protonated to NH₃ *via* NNH₂ and NHNH₂ intermediates, with little or no hydrazine formation.



However, the information currently available about the enzyme does not rule out a two-site mechanism (two Mo's or one Mo and one Fe) with bridged dinitrogen complexes reducing *via* bridged di-imide and hydrazine intermediates, and work continues on the chemistry of these types of complex ligand, prepared by oxidation of bridging hydrazine derivatives. The N—H protons of [μ-N₂H₂{Cr(CO)₅}]₂ undergo rapid H—D exchange and in the presence of catalytic amounts of base rapid and irreversible disproportionation to N₂ and [μ-N₂H₄{Cr(CO)₅}]₂ occurs.⁶⁴ A crystal structure of the THF solvate of [μ-N₂H₂{Cr(CO)₅}]₂ shows the di-imide ligand to have a *trans* configuration with an N—N bond length of 1.25 Å.⁶⁵ [Mo(CO)₅N₂H₄] is

⁵⁸ D. Sellmann, *Angew. Chem. Internat. Ed.*, 1974, **13**, 639. A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, and R. N. Whiteley, *Chem. Rev.*, 1973, **73**, 11.

⁵⁹ C. R. Brûlet and E. E. Van Tamelen, *J. Amer. Chem. Soc.*, 1975, **97**, 911.

⁶⁰ J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1975, **253**, 39.

⁶¹ J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1975, 983.

⁶² J. Chatt, *J. Organometallic Chem.*, 1975, **100**, 17.

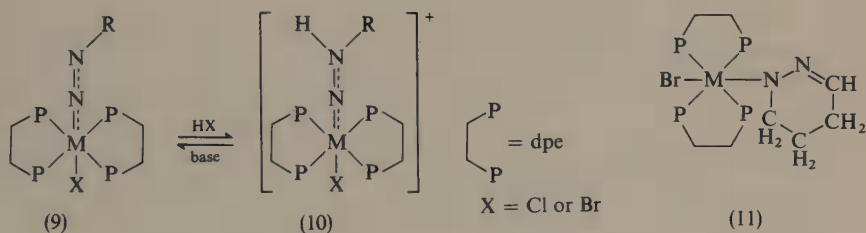
⁶³ J. Chatt, A. J. Pearman, and R. L. Richards, *J. Organometallic Chem.*, 1975, **101**, C45.

⁶⁴ D. Sellmann, A. Brandl, and R. Endell, *J. Organometallic Chem.*, 1975, **90**, 309.

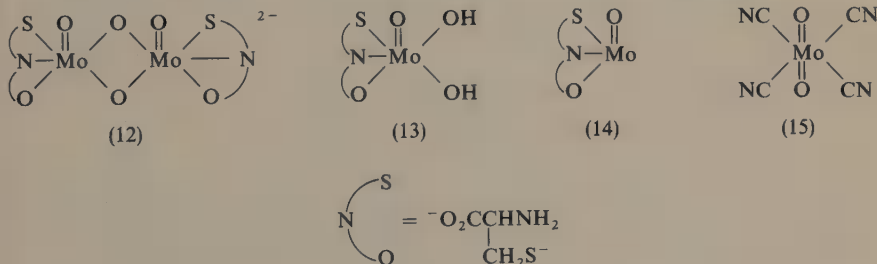
⁶⁵ G. Muttner, W. Gartzke, and K. Allinger, *J. Organometallic Chem.*, 1975, **91**, 47.

prepared from $[\text{Mo}(\text{CO})_6]$ and N_2H_4 , and controlled oxidation yields $[\mu\text{-N}_2\text{H}_2\{\text{Mo}(\text{CO})_5\}_2]$ which is less stable than its Cr or W analogues and readily disproportionates to the μ -hydrazine derivative and N_2 .⁶⁶

The formation of nitrogen-carbon bonds directly from dinitrogen is potentially a reaction of industrial importance and continues to be studied. Photochemical reaction of the dinitrogen complexes $[\text{M}(\text{N}_2)_2(\text{dpe})_2]$ ($\text{M} = \text{Mo}$ or W) with alkyl halides RX has been independently studied by two groups^{68,69} and shown to give alkylidiazenido (9) and alkylhydrazido(2-) (10) complexes, interconvertible by acid and base. X-Ray crystal structures of (9; $\text{R} = \text{C}_6\text{H}_{11}$, $\text{X} = \text{I}$, $\text{M} = \text{Mo}$)⁶⁹ and (10; $\text{R} = \text{Me}$, $\text{X} = \text{Br}$, $\text{M} = \text{W}$)⁶⁸ both show essentially linear $\text{M}-\text{N}-\text{N}$ systems with $\text{M}-\text{N}$ bond lengths of 1.95(1) and 1.768(14) Å, respectively. If the alkylation reaction is carried out in tetrahydrofuran as solvent, the tetrahydropyridazine complex (11) is formed, and can be isolated at its hydrobromide salt.⁷⁰ The four carbons of the pyridazine ring presumably originate from the THF, and the role of the methyl bromide is not clear; it may participate in removal of the THF oxygen as an alcohol.



Efforts continue to be directed towards the simulation of the action of nitrogenase using systems containing a dimeric molybdenum(v) cysteine complex (12) and a reducing agent, and the area has been reviewed.⁷¹ Such systems reduce acetylene to ethylene, and dinitrogen to ammonia in low yields. Ferredoxin model compounds such as $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{n-}$ ($n = 2-4$) apparently accelerate the transfer of electrons



⁶⁶ D. Sellmann, A. Brandl, and R. Endell, *J. Organometallic Chem.*, 1975, **97**, 229.

⁶⁷ J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 444.

⁶⁸ A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organometallic Chem.*, 1975, **84**, C11; F. F. March, R. Mason, and K. M. Thomas, *J. Organometallic Chem.*, 1975, **96**, C43.

⁶⁹ V. W. Day, T. A. George, and S. D. A. Isbe, *J. Amer. Chem. Soc.*, 1975, **97**, 4127.

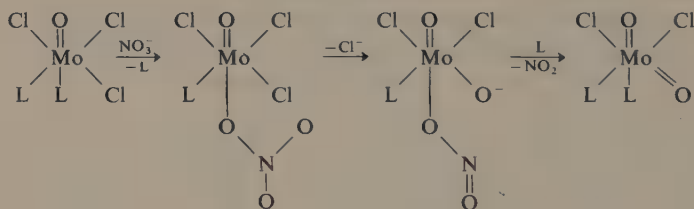
⁷⁰ A. A. Diamantis, J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1975, 27.

⁷¹ G. N. Schrauzer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 514.

from reductant to molybdenum and improve ethylene yields.⁷² Adenosine-5-triphosphate (ATP) is a requirement for the enzyme and also stimulates the model system. The ATP is postulated to facilitate removal of OH groups from the monomer (13) [formed from (12) in base] as phosphates and thereby increases the concentration of the active reduced Mo^{IV} species (14). Use of the tetracyano-oxo-Mo complex (15) as an alternative to (12) increases the nitrogen-fixing ability of the model system considerably, and yields of up to *ca.* 0.3 moles of ammonia per mole of molybdenum are quoted.⁷⁴

Electrochemical reduction of the Mo^V cysteine dimer shows that it undergoes a single four-electron reduction step to Mo^{III} products, and it is suggested that a monomeric Mo^{III} species is the catalytically active species.⁷⁵ A dextran-bound cysteine polymer (1.05 mmol cysteine per g dextran) forms a molybdenum complex analogous to (12) which shows no evidence for alkaline dissociation into monomers analogous to (13).⁷⁶ However, in the presence of borohydride the supposed complex reduces acetylene *ca.* 30 times faster than (12), possibly because the inert support serves to keep apart reduced catalytically-active species analogous to (14), preventing formation of inactive oxo-bridged dimers.

The nitrate ion is quantitatively converted into NO₂ and subsequently nitrogen(III) (probably $\dot{\text{N}}\text{O}$) by reaction with [MoOCl₃L₂] or [MoOCl₄L]⁻ [L = Ph₃PO or (Me₂N)₃PO] or [MoOCl₅]²⁻ and this has been advanced as a model for the molybdoenzyme nitrate reductase.⁷⁷ The kinetics of the overall reaction were studied by stopped-flow techniques and are consistent with the mechanism in Scheme 2.⁷⁷ However, unlike the enzyme the system is not catalytic, and reduces nitrite quantitatively to NO. Since O-bonding appears to be a prerequisite for the reduction of nitrate or nitrite, it is suggested that the protein stabilizes N-bonding of nitrite by hydrogen-bonding with the oxygens, preventing its reduction.⁷⁸



Scheme 2

Isocyanides, nitriles, or acetylenes are also substrates for nitrogenase, and the chemistry of these ligands bound to molybdenum has been studied. Both dinitrogen ligands of *trans*-[Mo(N₂)₂(dpe)₂] are displaced by methyl isocyanide to give *trans*-[Mo(MeNC)₂(dpe)₂]. One or both of the ligating isocyanides can be protonated at

⁷² K. Tano and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1975, **97**, 3404.

⁷³ G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. R. Robinson, *J. Amer. Chem. Soc.*, 1975, **97**, 6088.

⁷⁴ G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, and T. M. Vickney, *J. Amer. Chem. Soc.*, 1975, **97**, 7069.

⁷⁵ D. A. Ledwith and F. A. Schultz, *J. Amer. Chem. Soc.*, 1975, **97**, 6591.

⁷⁶ H. Susuki, S. Meshitsuka, T. Tabashima, and M. Ichikawa, *Chem. Letters*, 1975, **4**, 285.

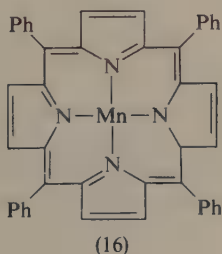
⁷⁷ C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *Nature*, 1974, **252**, 580.

⁷⁸ C. D. Garner, M. R. Hyde, and F. E. Mabbs, *Nature*, 1975, **253**, 623.

nitrogen to give complexes containing the carbyne-like ligands ---C---NHR .⁷⁹ Substituted benzonitriles displace only one dinitrogen from $[\text{Mo}(\text{N}_2)_2(\text{dpe})_2]$ to give $[\text{Mo}(\text{N}_2)(p\text{-XC}_6\text{H}_4\text{CN})(\text{dpe})_2]$ ($\text{X} = \text{NH}_2, \text{MeO}, \text{Me}, \text{H}, \text{Cl}, \text{or COMe}$), the latter being useful precursors for the synthesis of derivatives such as $[\text{MoCl}(\text{N}_2\text{COPh})(\text{dpe})_2]$ with N---C bonds.⁸⁰ Acetylene readily displaces the carbonyl ligands from the complexes $[\text{Mo}(\text{CO})_2(\text{S}_2\text{PPR}^i_2)_2]$ to give $[\text{MoCO}(\text{C}_2\text{H}_2)(\text{S}_2\text{PPR}^i_2)_2]$; but reaction with acid gives only *ca.* 20% yields of ethane from the acetylene.⁸¹

3 Group VII: Manganese, Technetium, and Rhenium

Manganese Porphyrin and Related Complexes.—Although the dioxygen-carrying capabilities of iron and cobalt complexes have been extensively investigated (see pp. 162 and 167), analogous manganese derivatives have only recently been studied in detail. Manganese porphyrin complexes were comprehensively reviewed in 1972.⁸² Manganese haemoglobin (MnHb) does not bind dioxygen reversibly and is irreversibly oxidized to $\text{Mn}^{\text{III}}\text{Hb}$,⁸³ and the manganese tetraphenylporphyrin (TPP) system also shows significant differences from comparable iron derivatives. Reduction of $[\text{Mn}^{\text{III}}\text{Cl}(\text{TPP})]$ with $[\text{Cr}_2(\text{acac})_4]$ in toluene gives the purple four-co-ordinate species $[\text{Mn}(\text{TPP}), 2\text{toluene}](16)$.⁸⁴ A partial X-ray crystal structure and magnetic measurements ($\mu_{\text{eff}} = 6.2 \text{ BM}$) suggest a high-spin configuration with the manganese lying out of the plane of the porphyrin ring. $[\text{Mn}(\text{TPP})]$ reacts with an excess of a base such as 2-methylimidazole (2-MeIm) to give $[\text{Mn}(\text{TPP})(2\text{-MeIm})]$, with no evidence for a six-co-ordinate species.⁸⁴ In contrast to its iron analogue, $[\text{Mn}(\text{TPP})(1\text{-MeIm})]$ does not react with dioxygen except to undergo very slow oxidation. It is suggested that the six co-ordination required for an O_2 -adduct cannot occur unless a transition to a low-spin state occurs, which is not possible with the porphyrin ligand system. However, $[\text{Mn}(\text{TPP})]$ does reversibly form an O_2 -adduct at -90°C in toluene-THF, although this has not yet been fully characterized.



⁷⁹ J. Chatt, A. J. L. Pompeiro, R. L. Richards, G. M. D. Royston, K. W. Muir, and R. Walser, *J.C.S. Chem. Comm.*, 1975, 512.

⁸⁰ T. Tatsumi, M. Hidai, and Y. Uchida, *Inorg. Chem.*, 1975, **14**, 2530.

⁸¹ J. W. McDonald, J. L. Corben, and W. E. Newton, *J. Amer. Chem. Soc.*, 1975, **97**, 1970.

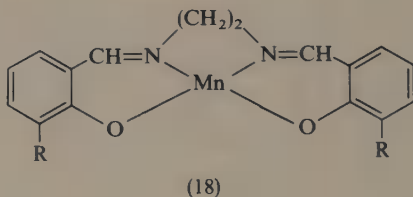
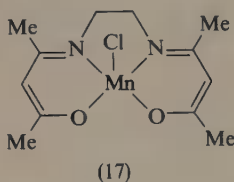
⁸² L. J. Boucher, *Coordination Chem. Rev.*, 1972, **7**, 289.

⁸³ C. Ball, R. C. Fisher, and B. M. Hoffmann, *Biochem. Biophys. Res. Comm.*, 1974, **59**, 146.

⁸⁴ B. Gonzalez, J. Kouba, S. Yee, C. A. Reed, J. K. Kirner, and W. R. Scheidt, *J. Amer. Chem. Soc.*, 1975, **97**, 3247.

Reaction of $[\text{Mn}(\text{TPP})(\text{py})]$ in toluene with O_2 at -80°C produces an apparently identical O_2 -adduct of stoichiometry $[\text{Mn}(\text{TPP})\text{O}_2]$, with displacement of pyridine.⁸⁵ E.s.r. spectra of the O_2 adduct were interpreted in terms of a manganese with three unpaired electrons, suggesting that the complex can formally be represented as $[\text{Mn}^{\text{IV}}(\text{TPP})(\text{O}_2^{2-})]$, with a 'sideways bound' O_2^{2-} ligand.⁸⁵

The structural distortions exhibited by five- or six-co-ordinate high-spin manganese(III) complexes provide the theme for several X-ray crystal structure determinations. The structures of $[\text{Mn}(\text{N}_3)(\text{TPP})]$ and $[\text{Mn}(\text{N}_3)(\text{MeOH})(\text{TPP})]$ ⁸⁶ show that the manganese ion is displaced *ca.* 0.18 Å further out of the plane in the five-co-ordinate derivative. A comparison of the structures of a number of related five-co-ordinate derivatives suggests that manganese(III) is displaced by *ca.* 0.25 Å from the plane in complexes of sterically non-hindered porphyrins. An even larger displacement (0.343 Å) occurs in the case of (17) with its less constrained quadridentate ligand system.⁸⁶ The structure of $[\text{Mn}(\text{acac})_2\text{N}_3]$ shows that the manganese is in fact six co-ordinate, as the azide ligands bridge adjacent $[\text{Mn}(\text{acac})_2]^+$ units producing infinite chains of pseudo-octahedral manganese ions.⁸⁷



The products of oxidation by dioxygen of five-co-ordinate manganese(III) Schiff base complexes such as $[\text{Mn}(\text{salen})(\text{H}_2\text{O})]^+$ (18; $\text{R} = \text{H}$) have not in the past been well characterized, μ -peroxo, di- μ -hydroxo, and di- μ -oxo structures having been proposed.⁸⁸ The situation has been clarified by detailed studies of the oxidation of the more soluble $[\text{Mn}(\text{Busalen})\text{H}_2\text{O}]\text{ClO}_4$ (18; $\text{R} = \text{s-butyl}$).⁸⁹ In the presence of base and dioxygen this gives a complex formulated as the manganese(IV) $[(\text{Busalen})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{Busalen})]\text{H}_2\text{O}$ (19). This is dimeric in CHCl_3 and the low magnetic moment (2.5 BM) is attributed to antiferromagnetic exchange between the manganese ions. A characteristic i.r. band in the region $640\text{--}650\text{ cm}^{-1}$ is assigned to the di- μ -oxo bridging system. Protonation of (19) with perchloric acid provides further evidence for the structure as hydrogen peroxide is formed, *via* the di- μ -hydroxo species $[(\text{Busalen})\text{Mn}(\mu\text{-OH})_2\text{Mn}(\text{Busalen})]$.⁸⁹

The preparation of manganese or iron tetraphenylporphyrin nitrosyl complexes by direct reaction with nitric oxide is dependent on the presence of secondary amine. Thus $[(\text{NO})(\text{amine})\text{Mn}(\text{TPP})]$ is prepared in 80% yield by reaction of $[\text{ClMn}(\text{TPP})]$

⁸⁵ C. J. Weschler, B. M. Hoffmann, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 5278.

⁸⁶ V. W. Day, B. R. Stults, E. L. Tasset, R. S. Maranelli, and L. J. Boucher, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 505.

⁸⁷ B. R. Stults, R. S. Maranelli, and V. W. Day, *Inorg. Chem.*, 1975, **14**, 722.

⁸⁸ H. S. Maslen and T. N. Wates, *J.C.S. Chem. Comm.*, 1973, 760; T. Matushita, T. Yarno, I. Masuda, T. Shomo, and K. Shinra, *Bull. Chem. Soc. Japan*, 1973, **46**, 1712.

⁸⁹ L. J. Boucher and C. G. Coe, *Inorg. Chem.*, 1975, **14**, 1289.

with NO in CHCl_3 with piperidine present.⁹⁰ Since it has now been shown that the same reaction can be achieved with the so-called N_2O_2 adducts, in reality the *N*-nitrosohydroxylamines $[\text{R}^1\text{R}^2\text{NNH}_2][\text{R}^1\text{R}^1\text{NNO}]$, their intermediate formation is advanced as an explanation for the amine specificity of the direct nitrosation reaction.⁹¹

Complexes with Metal-Metal Multiple Bonds.—The chemistry of complexes with metal-metal bonds has also been a feature of the manganese group, and as mentioned previously the literature to the end of 1974 has been comprehensively reviewed.⁴⁵

The electrochemistry of the octahalogenodimetallates $[\text{M}_2\text{Cl}_8]^{n-}$ ($\text{M} = \text{Tc}$ or Re ; $n = 2$ or 3) has been reported,⁹² and the processes $[\text{Tc}_2\text{Cl}_8]^{2-} + e \rightarrow [\text{Tc}_2\text{Cl}_8]^{3-}$ and $[\text{Re}_2\text{Cl}_8]^{2-} + e \rightarrow [\text{Re}_2\text{Cl}_8]^{3-}$ shown to be quasi-reversible with $E_{1/2}$ potentials (relative to SCE) of 0.140 and -0.840 V, respectively. Paramagnetic $[\text{Tc}_2\text{Cl}_8]^{3-}$ has an e.s.r. spectrum corresponding to one unpaired electron coupled to two ^{99}Tc nuclei with $I = 9/2$; the corresponding $[\text{Re}_2\text{Cl}_8]^{3-}$ anion is too unstable for e.s.r. spectra to be observed.⁹²

However, tertiary phosphine derivatives of both $[\text{Re}_2\text{X}_8]^{3-}$ and $[\text{Re}_2\text{X}_8]^{4-}$ anions have been prepared.⁹³ Rhenium(III) chloride or the anions $[\text{Re}_2\text{X}_8]^{2-}$ ($\text{X} = \text{Cl}$ or Br) react with alkyl or mixed alkyl-aryl tertiary phosphines to give species of stoichiometry $[\text{Re}_2\text{X}_5(\text{PR}_3)_3]$ or $[\text{Re}_2\text{X}_4(\text{PR}_3)_4]$, the extent of reduction depending on the degree of alkyl substitution of the phosphine. Thus MePh_2P and EtPh_2P give $[\text{Re}_2\text{X}_5(\text{RPh}_2\text{P})_3]$ and PET_3 gives $[\text{Re}_2\text{X}_4(\text{PET}_3)_4]$. The ditertiary phosphine $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dpe) does not reduce the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion and $[\text{Re}_2\text{Cl}_6(\text{dpe})_2]$ is formed,⁹⁴ and shown by a crystal structure determination⁹⁵ to have a di- μ -chloro bridge with an $\text{Re}-\text{Re}$ distance of $3.809(1)$ Å, too large for any metal-metal interaction.

The complex $[\text{Re}_2\text{Cl}_4(\text{PET}_3)_4]$ is quasi-reversibly oxidizable electrochemically to $[\text{Re}_2\text{Cl}_4(\text{PET}_3)_4]^+$ and $[\text{Re}_2\text{Cl}_4(\text{PET}_3)_4]^{2+}$, and $[\text{Re}_2(\text{PhCO}_2)_4]^{2+}$ can be reduced to $[\text{Re}_2(\text{PhCO}_2)_4]^+$.⁹⁶ The e.s.r. spectra of the monocations can be qualitatively correlated with one-electron energy diagrams based on MO and scattered wave $X\alpha$ calculations.

The sulphato-bridged $\text{Na}_2[\text{Re}_2(\text{SO}_4)_4]$ can be prepared in 90% yield by reaction of $[\text{ReCl}_8]^{2-}$ with sulphuric acid and sodium sulphate in diglyme. The structure is essentially similar to that of $[\text{Mo}_2(\text{SO}_4)_4]^{4-}$ (7) with an $\text{Re}-\text{Re}$ bond length of $2.214(1)$ Å.⁹⁷ Partial replacement of halide ions occurs when $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ is fused with NN' -diphenylbenzamidine with formation of $[\text{Re}_2\text{Cl}_4(\text{N}_2\text{CPh}_3)_4]$. The amidine ligands bridge the two rheniums and the $\text{Re}-\text{Re}$ bond length of 2.177 Å is the shortest yet observed.⁹⁸

⁹⁰ P. L. Piciulo, G. Rupprecht, and W. R. Scheidt, *J. Amer. Chem. Soc.*, 1974, **96**, 5293.

⁹¹ P. L. Piciulo and W. R. Scheidt, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 309.

⁹² F. A. Cotton and E. Pedersen, *Inorg. Chem.*, 1975, **14**, 383.

⁹³ J. R. Ebner and R. A. Walton, *Inorg. Chem.*, 1975, **14**, 1987.

⁹⁴ J. A. Jaeger, D. P. Murtha, and R. A. Walton, *Inorg. Chem. Acta*, 1975, **13**, 21.

⁹⁵ J. A. Jaeger, W. R. Robinson, and R. A. Walton, *J.C.S. Dalton*, 1975, 698.

⁹⁶ F. A. Cotton and E. Pedersen, *J. Amer. Chem. Soc.*, 1975, **97**, 303.

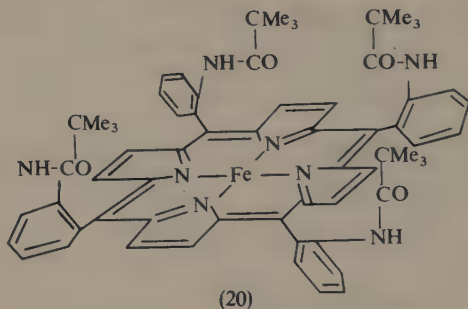
⁹⁷ F. A. Cotton, B. A. Frenz, and L. W. Shive, *Inorg. Chem.*, 1975, **14**, 649.

⁹⁸ F. A. Cotton and L. W. Shive, *Inorg. Chem.*, 1975, **14**, 2027.

4 Group VIIIA: Iron, Ruthenium, and Osmium

Synthetic Dioxygen Carriers.—A feature of the non-organometallic chemistry of iron has been the development of complexes that have dioxygen-carrying capabilities similar to those of haem proteins. Most of the model systems comprise ferrous iron surrounded by four co-planar nitrogens with a variety of nitrogeneous axial ligands, and progress to the end of 1974 has been described in two reviews.^{99,100}

A major problem with the model systems is the irreversible formation of μ -oxo-bridged dimers on treatment with dioxygen. This can be avoided by use of bulky ligands disposed to one side of the N_4 ligand, which prevents the irons getting close enough to form a dimer. Thus the ferrous complex of the 'picket-fence' porphyrin [*meso*-tetra(*aaaa*-*o*-pivalamidophenyl)porphyrin, TpivP] (20) adds two molecules of bases such as 1-methylimidazole (1-MeIm) to give diamagnetic six-co-ordinate derivatives which bind O_2 reversibly with displacement of one axial ligand.¹⁰¹ Although there were disorder problems, an X-ray crystal structure of $[Fe(O_2)TpivP](1-MeIm)]$ showed that the O_2 is bound 'end-on' with an $Fe-O-O$ angle of *ca.* 136° .¹⁰¹ The enthalpy of O_2 -binding in the solid state has been determined manometrically¹⁰² ($\Delta H^\circ = -15.6 \text{ kcal mol}^{-1}$), and comparison with natural haem proteins (ox myoglobin $\Delta H^\circ = -15 \text{ kcal mol}^{-1}$; human myoglobin $\Delta H^\circ = -13.4 \text{ kcal mol}^{-1}$) suggests the protein chains in the natural system do not contribute significantly to O_2 -binding.



An alternative to the 'picket-fence' approach has been to use substituted haem derivatives such as (21) where the axial base is attached to a pyrrohaem system with a similar geometry to the proximal histidine in myoglobin.^{103,104} These systems bind O_2 reversibly, and the kinetics of oxygenation can be studied as a function of the axial base and solvent polarity, which do not interfere. The rates of oxygenation closely resemble those of myoglobin, and the dependence of the O_2 'on'-rate on the axial base suggests that the natural system could control the rate of binding of O_2 by variation of the basicity of the proximal histidine.¹⁰⁴ Not all systems are based on

⁹⁹ F. Basolo, B. M. Hoffmann, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

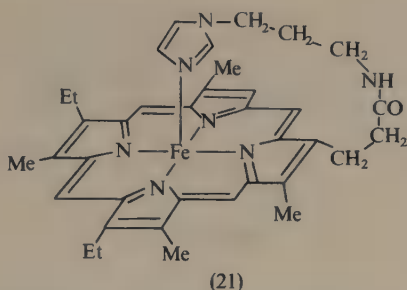
¹⁰⁰ T. H. Maugh, *Science*, 1975, **187**, 154.

¹⁰¹ J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Amer. Chem. Soc.*, 1975, **97**, 1427, and references therein.

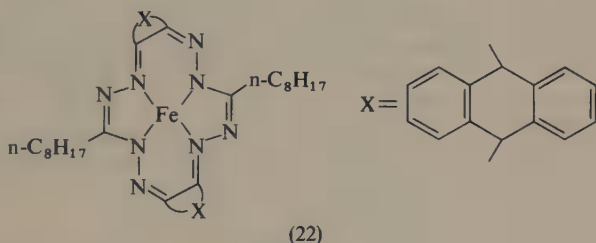
¹⁰² J. P. Collman, J. I. Brauman, and K. S. Suslick, *J. Amer. Chem. Soc.*, 1975, **97**, 7185.

¹⁰³ C. K. Chang and T. G. Traylor, *J. Amer. Chem. Soc.*, 1973, **95**, 5810.

¹⁰⁴ C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U. S. A.*, 1975, **72**, 1166.



porphyrin ligands, and the substituted octa-aza[14]annulene complex (22) also undergoes reversible oxygenation at low temperature. The X-ray crystal structure of (22) shows that the iron lies in a 4.5 Å deep pocket, between the 9,10-dihydroanthracene rings; the octyl groups are directed away from the iron.¹⁰⁵



Oxo-bridge formation can also be inhibited by oxygenation at low temperatures (−50 to −80 °C). [Fe(TPP)(l-MeIm)₂] is irreversibly oxidized at 25 °C but functions as an O₂-carrier at −80 °C. Oxygenation is almost complete in methylene chloride, but minimal in toluene, and the stabilization in polar solvents supports the formal representation of the O₂-adduct as [Fe^{III}(O₂[−])(TPP)(l-MeIm)].¹⁰⁶ Studies of the kinetics of oxygenation show that [Fe(TPP)(l-MeIm)] reacts at about the same rate with O₂ and l-MeIm, and the stability of the O₂-adduct is dependent on axial base, as for complex (20).¹⁰⁷ Attachment of [Fe^{II}(TPP)] to an inert solid support holds the irons apart and prevents dimer formation. The iron porphyrin is bound to silica *via* 3-imidazolylpropyl groups and binds O₂ reversibly at low temperature. However, the O₂ is only weakly chemisorbed with a *p*_{1/2} value of 0.4 Torr at −80 °C, compared with an extrapolated value of 0.14 Torr for human myoglobin at 0 °C.⁹⁹

Cytochrome P450 contains a haem iron prosthetic group but is functionally more complex than haemoglobin, acting as a dioxygen and electron-transport agent, and as an oxidation catalyst. Four distinct reaction states can be identified, corresponding to binding of the oxidizable substrate (sub) adjacent to the iron, reduction of the ferric cytochrome Fe^{III}(cyt), binding of O₂, and further reduction with

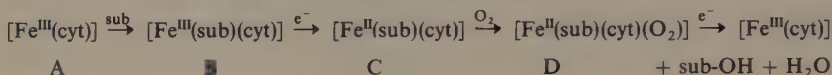
¹⁰⁵ R. G. Little, J. A. Ibers, and J. E. Baldwin, *J. Amer. Chem. Soc.*, 1975, **97**, 7049.

¹⁰⁶ C. J. Weschler, D. L. Anderson, and F. Basolo, *J.C.S. Chem. Comm.*, 1974, 757.

¹⁰⁷ C. J. Weschler, D. L. Anderson, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 6707.

¹⁰⁸ I. C. Gunsalus, S. G. Sligar, and P. G. Debrunner, *Biochem. Soc. Trans.*, 1975, **3**, 821; and preceding papers.

formation of hydroxylated substrate (sub-OH) and water and regeneration of $\text{Fe}^{\text{III}}(\text{cyt})$ (Scheme 3). E.s.r. spectra of the biological system suggest axial ligation by sulphur, and studies on model systems have accordingly been based on iron complexes with macrocyclic N_4 -donor and axial thiolate ligands.



Scheme 3

The five-co-ordinate species $[\text{Fe}(\text{SPh})(\text{TPP})]$ can be prepared from $[\{\text{Fe}(\text{TPP})\}_2\text{O}]$ and thiophenol, and has an e.s.r. spectrum with g values close to those of species B in Scheme 3.¹⁰⁹ In the presence of a base such as methylamine or ammonia, at low temperatures, an e.s.r. spectrum resembling that of species A is observed. An iron protoporphyrin dimethyl ester (PPDME) system forms the analogous $[\text{Fe}(\text{SC}_6\text{H}_4\text{p-NO}_2)\text{PPDME}]$, and the X-ray crystal structure shows the iron displaced *ca.* 0.43 Å out of the plane of the ligating porphyrin. Models for species C and D in Scheme 3 were synthesized by reaction of benzene solutions of $[\text{Fe}(\text{PPDME})]^{111}$ or $[\text{Fe}(\text{TpipP})]^{112}$ with an excess of crown-ether-solubilized thiol, which effects reduction to the ferrous state. Under CO a u.v. band at *ca.* 450 nm appears which corresponds to the anomalous Soret band which gives the cytochrome its name. If mercaptan rather than mercaptide is used, the Soret band appears at *ca.* 420 nm. In combination, these studies on model systems, while not conclusive, do offer confirmation that the ferric species A and B of cytochrome P450 do contain an axial thiolate ligand. However, the nature of the diamagnetic O_2 -binding species D is not yet clear.

Iron-Sulphur Cluster Systems.—Non-haem iron-sulphur proteins are implicated in biological processes as diverse as photosynthesis and nitrogen fixation. They can be classified according to the number of iron atoms present: Fe, 2Fe, 4Fe, and 8Fe proteins. X-Ray crystal structures of the 4Fe protein from *Chromatium* and the 8Fe protein from *P. aerogenes* show them to contain one and two $[\text{Fe}_4\text{S}_4(\text{S-cys})_4]$ clusters (S-cys = cysteinyl sulphur) respectively. Redox and spectral measurements show that the 4Fe proteins are predominantly of two types: the high potential protein (HiPIP; $E'_0 \sim +0.35$ V) from photosynthetic bacteria and the non-photosynthetic bacterial ferredoxins (Fd; $E'_0 \sim -0.4$ V). The complexes $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ (R = alkyl or aryl), containing structurally and spectrally analogous clusters, were synthesized some time ago, and work in this area up to the end of 1974 has been reviewed.¹¹³

The synthetic clusters are prepared in high yields from FeCl_3 , thiol, and NaHS in the presence of base, and an X-ray crystal structure (23) indicates that they are somewhat distorted from cubic symmetry.¹¹⁴ Polarography shows that the $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ clusters are members of the electron-transfer series $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{n-}$

¹⁰⁹ J. P. Collman, T. N. Sorrell, and B. M. Hoffmann, *J. Amer. Chem. Soc.*, 1975, **97**, 913.

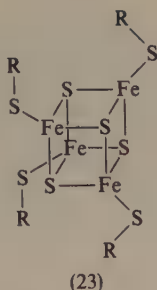
¹¹⁰ S. Koch, S. C. Tang, R. H. Holm, R. B. Frankel, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1975, **97**, 917.

¹¹¹ C. K. Chang and D. Dolphin, *J. Amer. Chem. Soc.* 1975, **97**, 5948.

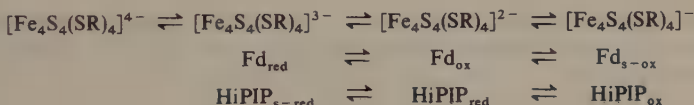
¹¹² J. P. Collman and T. N. Sorrell, *J. Amer. Chem. Soc.*, 1975, **97**, 4133.

¹¹³ R. H. Holm, *Endeavour*, 1975, **34**, 1.

¹¹⁴ B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3523.



where $n = 1, 2, 3$, or 4 .¹¹⁵ Magnetic and spectral studies indicate a close similarity between these states and those found in the biological systems as indicated by the columns in Scheme 4. However, the $3- \rightarrow 2-$ reduction step for the synthetic clusters is thermodynamically irreversible, with $E_{1/2}$ values considerably larger than for one-electron reduction of the ferredoxins. The water-soluble cluster $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{CH}_2\text{CO}_2)_4]^{6-}$ can, however, be reversibly reduced, and the potential associated with the one-electron step (-0.58 V *vs.* hydrogen electrode) is close to that of ferredoxins (Fd).¹¹⁶



Scheme 4

The structural unit of the Fe—S moiety of the 2Fe proteins has not been established by X-ray diffraction, but the synthetic model (24), prepared according to equation (5), has similar spectroscopic properties to the biological system.¹¹⁷

The $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ clusters undergo facile thiol exchange reactions, and this provides the basis of a method for the removal of intact iron-sulphur clusters from the proteins.¹¹⁵ Treatment of a 4:1 DMSO:H₂O solution of the 8Fe ferredoxin protein from *Clostridium pasteurianum* with a 35-fold excess of thiophenol gives a 95% recovery of the non-haem iron as $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$. The high DMSO content of the solution facilitates reaction by unfolding the protein chains. The Fe_2S_2 cores of 2Fe-ferredoxins can be similarly extruded using *o*-xylylenedithiol. However, conditions must be carefully controlled as the dinuclear complex readily dimerizes to a four-iron cluster, particularly at high pH and in the absence of an excess of thiol.¹¹⁸

Although Mössbauer, *e.s.r.*, and structural studies indicate that the synthetic clusters are good models for ferredoxins, the redox potentials are not comparable. These are clearly dependent on the peripheral groups on the clusters in the model systems and probably on the configuration of the peptide chains in the proteins. The

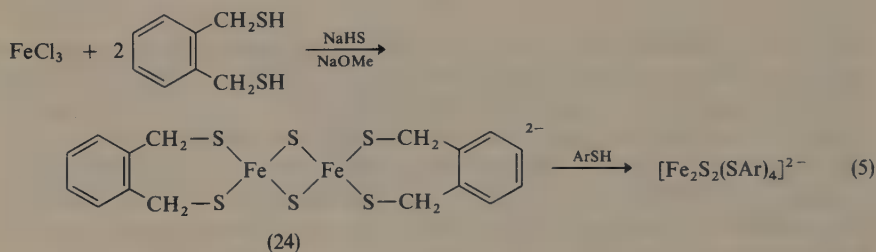
¹¹⁵ B. V. Pamphilis, B. A. Averill, T. Herskovitz, L. Que, and R. H. Holm, *J. Amer. Chem. Soc.*, 1974, **96**, 4159.

¹¹⁶ R. G. Job and T. C. Bruice, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 2478.

¹¹⁷ J. J. Mayerle, R. B. Frankel, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiker, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 2429.

¹¹⁸ L. Que, R. H. Holm, and L. E. Mortensen, *J. Amer. Chem. Soc.*, 1975, **97**, 463.

latter is certainly suggested by the accessibility of an additional super-reduced state, $\text{HiPIP}_{\text{S-red}}$, on denaturation of the HiPIP protein with DMSO.¹¹⁹ Any subtle distortions within the clusters caused by variation of the peripheral ligands should be reflected in the Fe—S stretching frequencies within the cluster. These can be enhanced in intensity by use of resonance Raman spectroscopy, and some recent results¹²⁰ suggest that the overall symmetry of the biological clusters is lower than that of the models. However, these differences are apparently too small to detect by X-ray diffraction as the structures of the biological and synthetic clusters are not significantly different.



Ruthenium Ammine Complexes.—Ruthenium ammine complexes continue to be a source of unusual and interesting chemistry, displacement of the water ligand of $[\text{RuA}_5(\text{H}_2\text{O})]^{2+}$ ($\text{A} = \text{NH}_3$) providing a readily accessible co-ordination site. It has been known for some time that $[\text{RuA}_5(\text{H}_2\text{O})]^{2+}$ reacts with N_2O to give $[\text{RuA}_5(\text{N}_2)]^{2+}$ via an unstable N_2O complex.¹²¹ The latter has now been isolated using high pressures of N_2O , and isotopic labelling using ^{15}NNO and N^{15}NO permits assignment of anion-dependent i.r. bands, in the regions 1945—1975 and 869—880 cm^{-1} , to the N_2O ligand.¹²² Force-constant calculations are consistent with an O-bonded N_2O ligand.

Nitrogen-metal to carbon-metal bonding isomerization has been observed for imidazole bound to $[\text{RuA}_5]^{2+}$.¹²³ HCN initially binds via nitrogen and then rapidly isomerizes to the carbon-bound species $[\text{RuA}_5\{\text{C}(\text{H})\text{N}\}]^{2+}$. In the presence of base a proton is lost, generating a cyano-complex which expels an NH_3 ligand to give the product ultimately isolated, polymeric $[\{\text{A}_4\text{Ru}(\text{CN})\}]_n$.¹²⁴ Xanthine derivatives (25) can also bind to $[\text{RuA}_5]^{2+}$ or $[\text{RuA}_5]^{3+}$ via N-7 or C-8, the bonding mode being a function of the substitution pattern of the xanthine and pH; C-bonding is favoured at low pH.¹²⁵ Electrochemical studies indicate that both N- and C-bonding stabilize Ru^{II} relative to Ru^{III} probably because both bonding modes transfer more π -electron density from metal to ligand in the Ru^{II} state.

¹¹⁹ R. Cummack, *Biochem. Biophys. Res. Comm.*, 1974, **58**, 974.

¹²⁰ S.-P. W. Tang, T. G. Spiro, C. Antaratitis, T. H. Moss, R. H. Holm, T. Herskovitz, and L. E. Mortensen, *Biochem. Biophys. Res. Comm.* 1975, **62**, 1.

¹²¹ J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 6476.

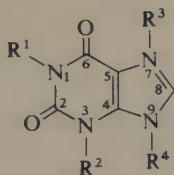
¹²² A. A. Diamantis, G. J. Sparrow, M. R. Snow, and T. R. Norman, *Austral. J. Chem.*, 1975, **28**, 1231.

¹²³ R. J. Sundberg, R. E. Shepherd, and H. Taube, *J. Amer. Chem. Soc.*, 1972, **94**, 6558.

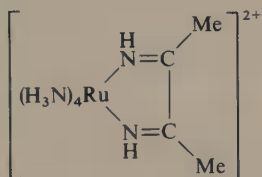
¹²⁴ S. S. Isred and H. Taube, *Inorg. Chem.*, 1975, **14**, 2561.

¹²⁵ M. J. Clarke and H. Taube, *J. Amer. Chem. Soc.*, 1975, **97**, 1397.

One NH_3 ligand of the Ru^{III} hexammines $[\text{RuA}_6]^{5+}$ can be deprotonated to NH_2 ($\text{p}K_a$ ca. 12.4) which reacts with dioxygen at pH 13 to give $[\text{RuA}_5(\text{NO})]^{3+}$, identified by a strong i.r. band at 1908 cm^{-1} [$\nu(\text{NO})$].¹²⁶ The NH_2 ligand of $[\text{RuA}_5(\text{NH}_2)]^{2+}$ is sufficiently nucleophilic to attack carbonyl carbons, and reaction with α -diketones, such as diacetyl, gives di-imine complexes (26).¹²⁷ Aldehydes RCHO react with $[\text{RuA}_6]^{3+}$ to give high yields of the nitrile complexes $[\text{RuA}_5(\text{NCR})]^{2+}$,¹²⁸ previously prepared from $[\text{RuA}_5(\text{H}_2\text{O})]^{2+}$ and nitrile.¹²⁹ The mechanism is not yet known, but probably does not involve the Ru^{III} complexes $[\text{RuA}_5(\text{NCR})]^{3+}$ as these hydrolyse rapidly in base to amide complexes.¹³⁰

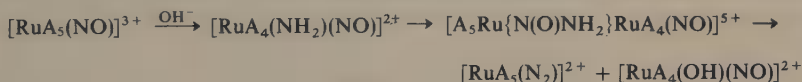


(25)



(26)

Treatment of $[\text{RuA}_5(\text{NO})]^{3+}$ with base produces $[\text{RuA}_5(\text{N}_2)]^{2+}$ (25%) and *cis*- and *trans*- $[\text{Ru}(\text{OH})\text{A}_5(\text{NO})]^{2+}$ (19%); the mechanism is believed to involve nucleophilic attack of an NH_2 ligand on the co-ordinated NO, as in Scheme 5.¹³¹ Radiolysis of $[\text{RuA}_5(\text{NO})]^{3+}$ in $\text{Bu}'\text{OH}$ generates the Ru^{II} alkylnitroso-complex $[\text{RuA}_5\{\text{N}(\text{O})\text{CH}_2\text{C}(\text{OH})\text{Me}_2\}]^{2+}$,¹³² the reaction probably proceeds *via* attack of the radical $\dot{\text{C}}\text{H}_2\text{C}(\text{OH})\text{Me}_2$ on $[\text{RuA}_5(\text{NO})]^{2+}$ generated by reaction of H atoms and e_{aq}^- with the Ru^{III} nitrosyl complex.¹³³



Scheme 5

5 Group VIIIB: Cobalt, Rhodium, and Iridium

Major areas which have been explored this year are dioxygen complexes, new structural properties of chelated complexes, and catalytic behaviour.

Dioxygen as a Ligand.—An understanding of the binding of dioxygen to cobalt in its complex compounds is of importance with respect to biological dioxygen carriers.¹³⁴ Of major interest is the charge distribution within the cobalt- O_2 moiety. The apportioning of this charge has been the subject of recent controversy, but this year

¹²⁶ S. D. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, 1975, **97**, 5012.

¹²⁷ I. P. Evans, G. W. Everett, and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1975, 319.

¹²⁸ K. Schug and G. P. Guengerich, *J. Amer. Chem. Soc.*, 1975, **97**, 4135.

¹²⁹ R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 1970, **9**, 227.

¹³⁰ A. W. Zarella and P. C. Ford, *Inorg. Chem.*, 1975, **14**, 42.

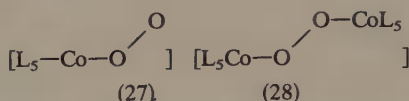
¹³¹ F. Bottomley, E. M. R. Kuremire, and S. G. Clarkson, *J.C.S. Dalton*, 1975, 1909.

¹³² J. N. Armor, R. Furman, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1975, **97**, 1737.

¹³³ J. N. Armor and M. Z. Hoffman, *Inorg. Chem.*, 1975, **14**, 444.

¹³⁴ F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

workers from three independent laboratories^{134,135} have interpreted e.s.r. spectra of mononuclear dioxygen adducts from Schiff-base or amine complexes of cobalt(II) in terms of almost complete transfer of an electron from cobalt to dioxygen, giving a formally $\text{Co}^{\text{III}}-\text{O}_2^-$ linkage. These results convincingly reinforce earlier similar interpretations of such charge transfer in substituted porphyrin complexes of cobalt. An X-ray photoelectron spectroscopic study of dioxygen adducts of Schiff base complexes of cobalt showed that the $\text{Co}2p_{3/2}$ binding energies increase by 0.9–1.9 eV when the Co^{II} complexes take up dioxygen, again indicating considerable electron transfer to dioxygen.¹³⁶



The reaction of O_2 with low-spin cobalt(II) complexes commonly gives terminally-bonded mononuclear (27) or dioxygen-bridged dinuclear (28) adducts, and physical studies on both classes of compound have been carried out. The $\text{Co}-\text{O}-\text{O}$ bond angle of 153.4° for $(\text{NEt}_4)_3[\text{Co}(\text{CN})_5(\text{O}_2)]$ ¹³⁷ is interpreted in terms of the $\text{Co}^{\text{III}}-\text{superoxide}$ linkage (27). The structure of the dinuclear analogue $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{5-}$ shows the 'staggered' structure (28) with an $\text{O}-\text{O}$ distance of 1.26 \AA , typical of μ -superoxide binding.¹³⁸ Examination of the electronic spectra of this complex and its ammine analogue $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{5+}$ has established low-spin, d^6 , Co^{III} centres for both compounds, and ligand field, ligand-to-metal charge transfer, and superoxide-localized transitions have been identified.¹³⁹ In particular, the bands due to metal-to-ligand charge transfer, terminating in the out-of-plane $\pi(\text{O}_2^-)$ orbital, have been assigned (486 and 672 nm, respectively) and a resonance Raman study confirms these assignments, the electronic transitions being coupled to the O_2^- bands (at 1104 and 1135 cm^{-1} , respectively) in the Raman spectra.¹⁴⁰

The structure of the five-co-ordinate precursor of the above dioxygen compounds, $[\text{Co}(\text{CN})_5]^{3+}$, shows that the yellow, solid form of this complex is a truly five-co-ordinate square-pyramidal compound, but possibly the green form, observed in aqueous solution, may have an apical H_2O molecule completing octahedral co-ordination.¹⁴¹

If tertiary phosphines replace cyanide as ligands to cobalt, a different mode of co-ordination of dioxygen results. Thus reaction of $[\text{Co}(\text{CN})_2(\text{PMe}_2\text{Ph})_3]$ with dioxygen gives the unsymmetrical dinuclear complex $[\text{Co}_2(\text{CN})_4(\text{PMe}_2\text{Ph})_5(\text{O}_2)]$ (29).¹⁴² While this mode of binding of dioxygen is unusual for dinuclear cobalt complexes, the $\text{O}-\text{O}$ distance (1.44 \AA) is in the range of such distances in analogous

¹³⁵ R. F. Howe and J. H. Lunsford, *J. Amer. Chem. Soc.*, 1975, **97**, 5156; D. Getz, E. Melamud, B. L. Silver, and Z. Dori, *ibid.*, p. 3847.

¹³⁶ J. H. Burness, J. G. Dillard, and L. T. Taylor, *J. Amer. Chem. Soc.*, 1975, **97**, 6080.

¹³⁷ L. D. Brown and K. N. Raymond, *Inorg. Chem.*, 1975, **14**, 2595.

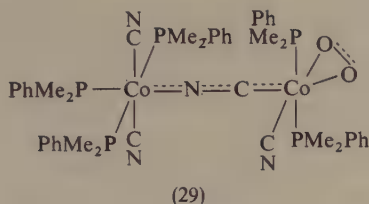
¹³⁸ F. R. Franczek, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, 1975, **14**, 611.

¹³⁹ V. M. Miskowski, J. L. Robbins, I. M. Treitel, and H. B. Gray, *Inorg. Chem.*, 1975, **14**, 2318.

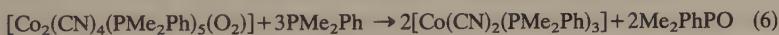
¹⁴⁰ T. C. Strekas and T. G. Spiro, *Inorg. Chem.*, 1975, **14**, 1421.

¹⁴¹ L. D. Brown and K. N. Raymond, *Inorg. Chem.*, 1975, **14**, 2590.

¹⁴² J. Halpern, B. L. Goodall, G. P. Khane, H. S. Lin, and J. J. Pluth, *J. Amer. Chem. Soc.*, 1975, **97**, 2301.



mononuclear complexes, *e.g.* $[\text{IrCl}(\text{CO})(\text{O}_2)(\text{PPh}_3)_2]$ (1.51 Å) and $(\text{Co}(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)_2(\text{O}_2))^+$ (1.42 Å). It is suggested that in (29) both cobalt atoms are formally Co^{III} , two electrons being transferred to the dioxygen *via* a ligand-bridged inner-sphere mechanism. The complex oxidizes PMe_2Ph in methanol solution [equation (6)].



The dioxygen adducts of iridium, $[\text{IrX}(\text{O}_2)(\text{CO})(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$), although quite stable under normal conditions, lose dioxygen on irradiation, even at 77 K. It is suggested that the photoinitiation process is triggered in an electronic state possessing iridium-to-phosphine charge-transfer character.¹⁴³ The X-ray structure of one such adduct, $[\text{IrO}_2\{\text{Ph}_2\text{PCH}_2\text{PPh}_2\}_2]\text{PF}_6$, has been re-determined.¹⁴⁴ The O—O bond distance now found (1.52 Å) is considerably shorter than that previously obtained, and in the range (1.41—1.52 Å) found in a variety of such complexes of cobalt, rhodium, and iridium; thus an apparent anomaly is resolved.

Dioxygen adducts of a number of other cobalt complexes have been prepared and investigated. Equilibrium studies on some chelating polyamine complexes of cobalt, which give μ -peroxo- μ -hydroxo-complexes with dioxygen and act as reversible dioxygen carriers, have shown a linear relationship between the logarithm of the stability constant of the dioxygen adduct and the sum of the $\text{pK}'\text{s}$ of the atoms ligating the cobalt ion.¹⁴⁵ This relationship allows prediction of the tendency of cobalt complexes to form stable dioxygen adducts. In particular it shows that the symmetrical and unsymmetrical ethylenediaminediacetic acids form quite stable dioxygen complexes in an appropriate pH range, although they contain only two basic nitrogen atoms, rather than the three which had previously been considered necessary.

Chelate Complexes of Biological Relevance. In a study of the interactions of metal ions and nucleotides, cytosine 5'-monophosphate (CMP) gave a polynuclear cobalt complex, $[\text{Co}(\text{CMP})(\text{H}_2\text{O})]_n\text{H}_2\text{O}$, which has tetrahedral Co^{II} bound to two oxygen atoms of a bridging phosphate group and N-3 of the pyrimidine.¹⁴⁶ Cobalt(III) complexes of azophenols have been prepared and their relevance to azotyrosine-modified enzymes, which may form exchange-inert Co^{III} complexes, is noted.¹⁴⁷ The X-ray structure of $[\text{Co}(\text{tren})(\text{gly})]^{2+}$ [$\text{tren} = \text{tris-(2-aminoethyl)amine}$, $\text{gly} = \text{glycine}$], formed by the hydrolysis of a glycine ester with $[\text{Co}(\text{tren})(\text{OH})(\text{H}_2\text{O})]^{2+}$, shows that

¹⁴³ G. L. Geoffroy, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 3933.

¹⁴⁴ M. Laing, M. J. Nolte, and E. Singleton, *J. Amer. Chem. Soc.*, 1975, **97**, 6396.

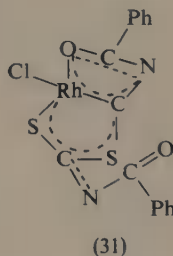
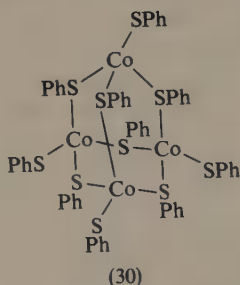
¹⁴⁵ G. McLendon and A. E. Martell, *J.C.S. Chem. Comm.*, 1975, 223.

¹⁴⁶ G. R. Clark and J. D. Orbell, *J.C.S. Chem. Comm.*, 1975, 697.

¹⁴⁷ W. I. White and J. I. Legg, *J. Amer. Chem. Soc.*, 1975, **97**, 3937.

the glycine is co-ordinated with its nitrogen atom *trans* to the tertiary amine of tren, and the tren ligand forms three diamine rings with two *K* and one *K'* conformations. This structure relates to specific hydrolysis of peptides by cobalt(III) complexes.¹⁴⁸ In a cobalt(III) carboxypeptidase A complex the magnetic moment ($\mu_{\text{eff}} = 4.77$ BM) and intensity of the principal visible absorption band (555.5 nm, $\epsilon = 150$) are considered compatible with a five-co-ordinate cobalt centre.¹⁴⁹ Cobalt complexes containing the corrin inner ring structure have been obtained by abstraction of hydride with a quinone, or other reagents, from bis(β -iminoamine)cobalt(II) complexes containing 14-, 15-, or 16-membered rings.¹⁵⁰

Complexes of Sulphur Ligands.—Some novel polynuclear cobalt complexes with bridging sulphur groups have been characterized. The tetrameric cluster compound (30) has a Co_4S_{10} framework of effectively T_d symmetry with bridging angles at S of 113° .¹⁵¹ A monosulphur-bridged, dinuclear complex $[(\text{CN})_5\text{CoSCo}(\text{CN})_5]^{6-}$ which is easily hydrolysed has been prepared from $[\text{Co}(\text{CN})_5]^{3-}$ and sulphur.¹⁵² Dinuclear thio-bridged complexes with dithiocarbamato- or *NN'*-ethylene-bis(thiosalicylaldiminato)-ligands have been prepared, and structural, spectroscopic and magnetic properties determined.¹⁵³ Oxidation of the complex $[\text{Co}(\text{en})_2(\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$ with Np^{VI} gives a novel cobalt(III) disulphide complex, $[\text{Co}(\text{en})_2\{\text{S}(\text{SCH}_2\text{CH}_2\text{NH}_3)\text{CH}_2\text{CH}_2\text{NH}_2\}]^{4+}$. A radical dimer intermediate is proposed.¹⁵⁴



A novel terdentate ligand is formed by the condensation of two benzoyl isothiocyanate molecules in the presence of $[\text{RhCl}(\text{PPh}_3)_3]$ (31).¹⁵⁵

The triply-bridged μ -chloro- μ -phenylthio-complex $[\text{Ir}_2\text{H}_2\text{Cl}(\text{SPh})_2(\text{PPh}_3)_4]$ has been prepared by reaction of $[\text{IrHCl}(\text{SPh})(\text{PPh}_3)_2]_2$ with AgClO_4 in acetone.¹⁵⁶ Thioformato-complexes $[\text{Ir}(\text{S}_2\text{CH})\text{X}(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}$ or Br) have been prepared, and the diagnostic spectral properties of this ligand attached to various metals given.¹⁵⁷

¹⁴⁸ Y. Mitsui, J. Watanabe, Y. Iitaka, and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 280.

¹⁴⁹ R. C. Rosenberg, C. A. Root, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 21.

¹⁵⁰ S. C. Tang and R. H. Holm, *J. Amer. Chem. Soc.*, 1975, **97**, 3359.

¹⁵¹ I. G. Dance and J. C. Calabrese, *J.C.S. Chem. Comm.*, 1975, 762.

¹⁵² P. S. Poskozim, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2342.

¹⁵³ A. R. Hendrickson, R. L. Martin, and D. Taylor, *J.C.S. Dalton*, 1975, 2182; M. F. Corrigan, K. S. Murray, R. M. Sheahan, B. O. West, G. D. Fallon, and B. M. Gatehouse, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 625.

¹⁵⁴ M. Woods, J. C. Sullivan, and E. Deutsch, *J.C.S. Chem. Comm.*, 1975, 749.

¹⁵⁵ C. M. Lowie, J. A. Ibers, Y. Ishii, K. Itoh, I. Matsuda, and F. Ueda, *J. Amer. Chem. Soc.*, 1975, **95**, 4748.

¹⁵⁶ P. J. Roberts, G. Ferguson, and C. V. Senoff, *J. Organometallic Chem.*, 1975, **94**, C26.

¹⁵⁷ S. D. Robinson and A. Sahajpal, *J. Organometallic Chem.*, 1975, **99**, 665.

Chelating Phosphine Complexes.—This work involves primarily rhodium and iridium. Large-ring co-ordination complexes with *trans*-chelate phosphine ligands have recently been synthesized and structural parameters have now been determined for *trans*-[IrCl(CO){Bu^tP(CH₂)₁₀PBu^t₂}] and [RhCl(CO){Bu^tP(CH₂)₁₀PBu^t₂}]₂. The former has a 13-atom ring and the latter two μ -diphosphines forming a 26-membered ring; the phosphorus atoms are *trans* at the metal centres. The conformational properties of the rings are discussed.¹⁵⁸

Some *o*-metallated complexes [Ir(CO){PBu^t₂(C₆H₄O)}{PBu^t₂(C₆H₄OX-2)}] (X = H or Me) give (X = H) a blood-red paramagnetic ($\mu_{\text{eff}} = 1.73$ BM) iridium(II) complex *trans*-[Ir{PBu^t₂(C₆H₄O)}₂] on exposure to air. A hydrido-complex [IrH{PBu^t₂(C₆H₄O)}₂] is formed from this and dihydrogen, which reverts to its congener on exposure to air. A benzene solution of *trans*-[Ir{PBu^t₂(C₆H₄O)}₂] slowly gives, in air, the purple C-metallated compound [Ir{PBu^t₂(C₆H₄O)}{PBu^t(C₆H₄O)(CMe₂CH₂)}].¹⁵⁹ Another paramagnetic Ir^{II} complex, [Ir(O₂CR)₂(AsPh₃)(CNC₆H₄Me-*p*)] ($\mu_{\text{eff}} = 1.67$ BM, e.s.r. *g* values at 2.039 and 2.015), has been prepared by treatment of [IrH₃(AsPh₃)₂(CNC₆H₄Me-*p*)] with *p*-chlorobenzoic acid.¹⁶⁰

Reactions of Co-ordinated Ligands and Catalysis.—When co-ordinated to [M(NH₃)₅]³⁺ (M = Co, Rh, or Ir) organic nitriles are activated towards nucleophilic attack. Thus reduction of nitriles by BH₄⁻, Michael addition of carbanions to acrylonitrile (M = Co), or base hydrolysis of acetonitrile or benzonitrile (M = Co, Rh, or Ir) are all greatly accelerated by co-ordination to these metal centres.¹⁶¹ The complex [Co(NH₃)_nNO]²⁺, bound within a Y-type zeolite, is a catalyst for the conversion of NO and NH₃ into N₂ and H₂O at temperatures above 50 °C.¹⁶² This effect relates to the catalysed reduction of oxides of nitrogen from effluent gas streams by ammonia. The compounds [IrClX(NO)(CO)(PPh₃)₂] undergo an apparent electrophilic attack on the 'NO' ligand by dioxygen to give nitrate-complexes [IrClX(NO₃)(CO)(PPh₃)₂]; the rate of oxidation decreases with X in the order X = I > Br > Cl > NCS > NCO > N₃.¹⁶³

Asymmetric hydrogenation using rhodium complex catalysts continue to receive attention. The catalyst [Rh(cyclo-octa-1,5-diene){1,2-bis(*o*-anisyl(phenyl)phosphino)ethane}]⁺ induced optical purity in excess of 95–96% in the reduction of α -acylamidoacrylic acids.¹⁶⁴ Similarly, high optical yields have been obtained in the reduction of α -ethylstyrene and *N*-acetamidoacrylic acid derivatives with a rhodium complex of *trans*-1,2-bis(diphenylphosphino)cyclohexane, and related reductions occur using isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane as a ligand.¹⁶⁵

¹⁵⁸ F. C. March, R. Mason, B. L. Shaw, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1975, 584.

¹⁵⁹ H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J.C.S. Dalton*, 1975, 1690.

¹⁶⁰ A. Araneo, F. Morazzoni, and T. Napoletano, *J.C.S. Dalton*, 1975, 2039.

¹⁶¹ I. I. Creaser and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1975, 974; A. W. Zanella and P. C. Ford, *Inorg. Chem.*, 1975, **14**, 42, 700.

¹⁶² K. A. Windhorst and J. H. Lunsford, *J.C.S. Chem. Comm.*, 1975, 852.

¹⁶³ M. Kubota and D. A. Philips, *J. Amer. Chem. Soc.*, 1975, **97**, 5638.

¹⁶⁴ W. S. Knowles, M. J. Sabachy, B. D. Vineyard, and J. Weinkauff, *J. Amer. Chem. Soc.*, 1975, **97**, 2567.

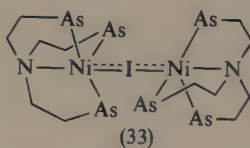
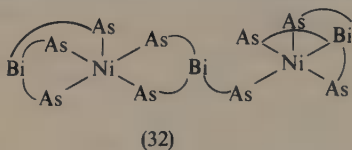
¹⁶⁵ M. Tanaka and I. Ogata, *J.C.S. Chem. Comm.*, 1975, 735; T. P. Dang, J. C. Poulin, and H. B. Kagan, *J. Organometallic Chem.*, 1975, **91**, 105.

Rhodium(III) chloride acts as a homogeneous catalyst for isotopic hydrogen exchange in deuteration of aromatic compounds or alkanes.¹⁶⁶ Reduction of dinitrogen to ammonia has been catalysed by aqueous acidic solutions of rhodium(III) or iridium(III) chloride. The reaction of a 1:3 mixture of dinitrogen and dihydrogen in presence of a reducing agent (TiCl_3 or SnCl_2 in 10 molar excess) gives yields of ammonia in the range 0.1–0.4 moles per mole of metal.¹⁶⁷

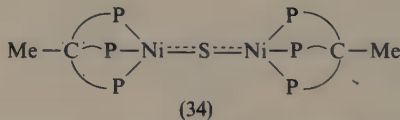
6 Group VIIC: Nickel, Palladium, and Platinum

Complexes of polydentate, often macrocyclic, ligands continue to be a feature of the chemistry of nickel.

Complexes of Multidentate Ligands.—Square-pyramidal complexes with, for the first time, nickel–bismuth bonds have been prepared from tris-(*o*-dimethylarsinophenyl)bismuthine (bitas), $[\text{NiX}(\text{bitas})]$ ($\text{X} = \text{halide}$) and $[\text{Ni}_2(\text{bitas})_3]^{4+}$. In the latter complex, bitas functions as a terdentate and a quadridentate ligand (32). 1,3-Bis(dimethylstibino)propane (dmsp) gives square-pyramidal complexes $[\text{NiX}(\text{dmsp})_2]\text{ClO}_4$.¹⁶⁸ Trigonal-bipyramidal stereochemistry is shown by $[\text{NiI}(\text{NCH}_2\text{CH}_2\text{NMe}_2)_3]\text{I}$.¹⁶⁹ The complex $[\text{NiI}(\text{nas})]\text{BPh}_4$ [$\text{nas} = \text{tris}(2\text{-diphenylarsinoethyl})\text{amine}$] reacts with NaBH_4 in ethanol to give a dimeric compound of nickel(I) (33) with a linear Ni—I—Ni bridge. This unit allows antiferromagnetic interaction between metal atoms.¹⁷⁰



A novel linear Ni—S—Ni system occurs in (34), prepared by reaction of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, H_2S , and 1,1,1-tris(diphenylphosphinomethyl)ethane. The short Ni—S (2.034 Å) distance indicates a high π -component in the Ni—S bonds, in keeping with the linear Ni—S—Ni system and diamagnetism of the complex.¹⁷¹



Five-co-ordinate complexes, particularly of nickel, can have square-pyramidal or trigonal-bipyramidal structure depending on the ligating atoms. The ligand $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_3\text{N}$, however, having the NP_3 donor set, appears to confer exclusively

¹⁶⁶ M. R. Blake, J. L. Garnett, I. K. Gregor, W. Hannan, K. Hoa, and M. A. Long, *J.C.S. Chem. Comm.*, 1975, 930.

¹⁶⁷ M. T. Khan and A. E. Martell, *Inorg. Chem.*, 1975, **14**, 938.

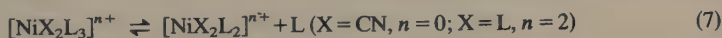
¹⁶⁸ W. Levason, C. A. McAuliffe, and S. G. Murray, *J.C.S. Chem. Comm.*, 1975, 164; R. J. Dickenson, W. Levason, C. A. McAuliffe, and R. V. Parish, *ibid.*, p. 272.

¹⁶⁹ P. L. Orioli and N. Nardi, *J.C.S. Chem. Comm.*, 1975, 229.

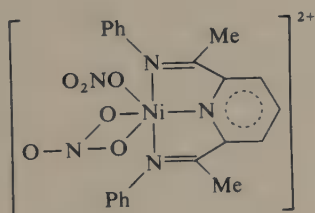
¹⁷⁰ L. Sacconi, P. Dapporto, and P. Stoppioni, *J. Amer. Chem. Soc.*, 1975, **97**, 5595.

¹⁷¹ C. Mealli, S. Midollini, and L. Sacconi, *J.C.S. Chem. Comm.*, 1975, 765.

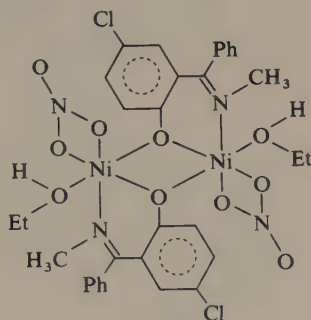
trigonal-pyramidal geometry upon nickel(II).¹⁷² This geometry is assigned to the complexes $[\text{Ni}(\text{CN})_2\text{L}_3]$ and $[\text{NiL}_5]^{2+}$ (L = tertiary phosphine or phosphite) which, in common with many five-co-ordinate complexes, are labile in solution giving an equilibrium of the type (7). The factors determining the equilibrium position are discussed in terms of the electronic spectra of the complexes.¹⁷³ The ligand tetars, $ms\text{-Me}_2\text{As}(\text{CH}_2)_3\text{As}(\text{Ph})\text{CH}_2\text{As}(\text{Ph})(\text{CH}_2)_3\text{AsMe}_2$, gives square-pyramidal complexes of type $[\text{MX}(\text{tetars})]^+$ ($\text{M} = \text{Ni}^{\text{II}}, \text{Pd}^{\text{II}}, \text{or Pt}^{\text{II}}$) whose absorption and circular dichroism spectra are interpreted in terms of the orbital energy ordering $d_{xy} > d_{xz} > d_{yz} > d_{z^2} > d_{x^2-y^2}$.¹⁷⁴



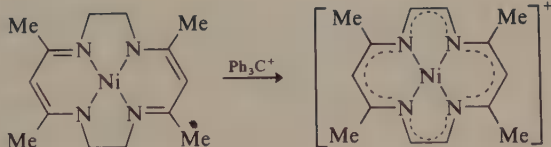
Synthesis of macrocyclic-ligand complexes often involves a condensation reaction between a carbonyl compound and an amine function in the presence of, or in the co-ordination sphere of, the metal. Many further examples of this type of system have appeared this year.¹⁷⁵ A Schiff-base complex of this type, with a planar N_3 donor set (35), also has both uni- and bi-dentate nitrato-groups.¹⁷⁶ Some new examples of dimeric Schiff-base complexes of nickel(II) have been prepared (36) and show intermolecular anti-ferromagnetic behaviour.¹⁷⁷



(35)



(36)



(37)

¹⁷² M. D. Vaira and L. Sacconi, *J.C.S. Dalton*, 1975, 493.

¹⁷³ E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, 1975, **14**, 1922.

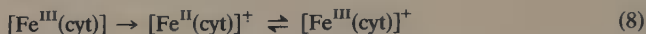
¹⁷⁴ B. Bosnich, W. G. Jackson, and S. T. D. Lo, *Inorg. Chem.*, 1975, **14**, 2998.

¹⁷⁵ D. B. Bonfoey and G. A. Melson, *Inorg. Chem.*, 1975, **14**, 304; N. F. Curtis, *J.C.S. Dalton*, 1975, 87, 91; R. Cheney, L. E. Heyman, and E. L. Blinn, *Inorg. Chem.*, 1975, **14**, 441; P. Domiano, A. Musatti, and N. Nardelli, *J. C. S. Dalton*, 1975, 295; J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 1881; M. J. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Amer. Chem. Soc.*, 1975, **97**, 192.

¹⁷⁶ E. C. Alyen, G. Ferguson, and R. J. Restivo, *Inorg. Chem.*, 1975, **14**, 2491; P. H. Merrell, *J. C. S. Chem. Comm.*, 1975, 269.

¹⁷⁷ R. J. Butcher and E. Sinn, *J.C.S. Chem. Comm.*, 1975, 832.

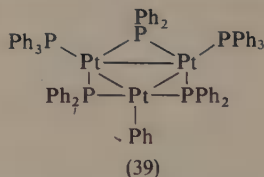
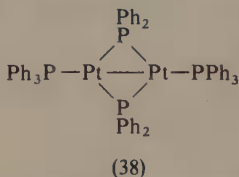
Macrocyclic bis(β -iminoamine) complexes of nickel(II) (see also copper and cobalt) containing 14-membered rings are converted into the delocalized radical cation (37) by oxidative dehydrogenation.¹⁷⁸ This has an e.s.r. signal of more than 80 lines which has been analysed in terms of a $^2B_{1u}$ ground state with an essentially $Ni^{II}-L^+$ (15π) system; that is, extensive ligand delocalization of the unpaired electron. This formalism is similar to that used to describe certain porphyrin cation radicals, one of which, $[Ni^{II}(TPP)]^+$ undergoes reversible electron transfer to give $[Ni^{III}(TPP)]^+$. This process has been likened to a suggested mechanism of electron transfer in cytochromes [equation (8)].¹⁷⁹



The above oxidative dehydrogenation method has been used extensively to convert other, larger ring, complexes into less saturated derivatives.¹⁷⁸ The base-promoted reduction of nickel(II) complexes of macrocyclic ligands gives nickel-macrocyclic radical species which undergo a number of other reactions and are suggested as intermediates in macrocyclic amine-complex reactions.¹⁸⁰

Zerovalent Complexes.—Complexes of nickel, palladium, and platinum in the zero oxidation state, particularly with tertiary phosphine ligands, continue to be prepared and their reactions studied. New examples are $[Pt\{P(CF_3)Ph_2\}_3]$,¹⁸¹ bis-[1,2-bis(difluorophosphino)cyclohexane]nickel(0),¹⁸² and $[Pt\{MeC(CH_2PPh_2)_3\}(PR_3)]$ $R = \text{alkyl, aryl, F, NMe}_2, \text{ or OPh}$.¹⁸³

Heating $[Pt(PPh_3)_4]$ in benzene gives the cluster compounds (38) and (39).¹⁸⁴ The reactions of ethane-1,2-dithiol, 2-(methylthio)ethanethiol, and 2-(methylthio)ethane disulphide with $[M(PPh_3)_4]$ ($M = Ni, Pt, \text{ or } Pd$) have been studied, and $[Pt(SCH_2CH_2S)_2(PPh_3)_2]$, $[Pd_2(SCH_2CH_2S)_4(PPh_3)_2]$, and $[Ni(SCH_2CH_2S)(Ph_2PCH_2CH_2PPh_2)]$ prepared.^{185a} By using an excess of halogen and short reaction times, the addition of halogens to $[Pt(PPh_3)_4]$ has been shown to give exclusively *trans*- $[PtX_2(PPh_3)_2]$ ($X = Cl, Br, \text{ or } I$) as the initially formed species.^{185b} The commonly observed products from such reactions are the *cis*-complexes formed by isomerization in the presence of free phosphine, avoided by the



¹⁷⁸ M. Millar and R. H. Holm, *J.C.S. Chem. Comm.*, 1975, 169; S. C. Tang and R. H. Holm, *J. Amer. Chem. Soc.*, 1975, **97**, 3351.

¹⁷⁹ D. Dolphin and R. H. Felton, *Accounts Chem. Res.*, 1974, **7**, 26; T. Nien and I. Fujita, *J. Amer. Chem. Soc.*, 1975, **97**, 5288.

¹⁸⁰ E. K. Barefield and M. T. Mocella, *J. Amer. Chem. Soc.*, 1975, **97**, 4238.

¹⁸¹ T. G. Attig, M. A. A. Beg, and H. C. Clark, *Inorg. Chem.*, 1975, **14**, 2986.

¹⁸² N. R. Zack, K. W. Morse, and J. G. Morse, *Inorg. Chem.*, 1975, **14**, 3131.

¹⁸³ J. Chatt, R. Mason, and D. W. Meek, *J. Amer. Chem. Soc.*, 1975, **97**, 3826.

¹⁸⁴ N. J. Taylor, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1975, 448.

¹⁸⁵ (a) B. Ranchfuss and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1975, **97**, 3386; (b) R. C. Stonfer, *ibid.*, p. 195; (c) K. B. Dillon, T. C. Waddington, and D. Younger, *J.C.S. Dalton*, 1975, 790; (d) J. F. Plummer and E. P. Schram, *Inorg. Chem.*, 1975, **14**, 1505; (e) K. Maeda, I. Moritani, Y. Hosokawa, and S. I. Murakashi, *J.C.S. Chem. Comm.*, 1975, 689; (f) M. Foa and L. Cassar, *J.C.S. Dalton*, 1975, 2572.

above reaction conditions. $[M(PPh_3)_4]$ ($M = Ni, Pt, \text{ or } Pd$) react with liquid HCl to give *cis*- $[MCl_2(PPh_3)_2]$,^{185c} with $TiCl_4$ ($M = Pt$) to give an adduct with $Pt-Ti$ bonds,^{185d} and with ketoximes in the presence of dioxygen ($M = Pd$) to give nitriles and aldehydes.^{185e} The mechanism of oxidative addition of aryl halides to $[Ni(PPh_3)_4]$ has been investigated.^{185f}

Oxidation State One.—Examples of platinum(I) and palladium(I) complexes are still rare (see Chapter 8, p. 207).^{186a,b} Electrochemical and e.s.r. studies of dithiolene complexes of palladium and platinum indicate that paramagnetic and presumably monomeric complexes of Pd^I and Pt^I are formed with these ligands.¹⁸⁷

Nuclear Magnetic Resonance Studies.—N.m.r. spectroscopy continues to be a powerful tool in the study of palladium and platinum complexes. The platinum(0) complexes $[Pt(\text{triphos})(PR_3)]$ [$\text{triphos} = MeC(CH_2PPh_2)_3$] mentioned above have $^1J(^{195}Pt-^{31}P(R_3))$ values larger than corresponding values in *trans*-platinum(II) (twice) and *cis*-platinum(II) (ca. 55% greater) complexes. $J(^{31}P, ^{31}P)$ values are also higher than in platinum(II) complexes. These differences are considered to be caused by the steric constraint of the triphos ligand which confers relatively low *s*-character in the Pt -triphos bonds and correspondingly high *s*-character in the $Pt-PR_3$ bonds.¹⁸³ The $^1J(^{195}Pt-^{31}P)$ values for *cis*- $[PtCl_2(R_2PCH_2CH_2PPh_2)]$ ($R = CF_3$ or Ph) show a strong dependence on substituents at phosphorus.^{188a} The values of $J(^{195}Pt, ^{13}C)$ and $J(^{195}Pt, ^{19}F)$ for platinum complexes of carbon monoxide^{188b} or SCF_3 ^{188c} have been discussed in terms of *trans*-influence of hydride and halide co-ligands.

The first values of $J(^{195}Pt, ^{77}Se)$ and $J(^{195}Pt, ^{125}Te)$ have been reported. They decrease markedly in the order $Cl > Br > I$ in the compounds $[PtX_3(SeMe_2)]^-$, $[PtX_5(SeMe_2)]^-$ and $[PtX_3(TeMe_2)]^-$ ($X = Cl, Br, \text{ or } I$).^{188d} Values of $^2J(^{195}Pt, ^{195}Pt)$ have been determined for the complexes $[PtCl_4(PBu_3)_2]$ and $[Pt_2I_4(PBu_3)_2]$.^{188e}

The mode of bonding of SCN groups (whether N or S ligation) has been a subject of interest and controversy for many years. Recently n.m.r. spectroscopy and X-ray crystallography has been used to determine the binding of the SCN group to platinum and palladium. In the platinum case the linkage isomers of $[Pt(CNS)_2(SMe_2)_2]$ (no implied N or S bonding) have been identified from coupling patterns of the 1H - $\{^{195}Pt\}$ INDOR spectra, and it is thought likely that ^{195}Pt chemical shifts will provide a means of distinguishing isomers.^{189a} The ^{31}P n.m.r. spectra of *cis*- $[PtX_2\{P(OPh)_3\}_2]$ ($X = CNS$ or $C^{15}NS$) show the independent existence of linkage isomers in solution.^{189b} An X-ray study of the complexes $[Pd(CNS)_2\{Ph_2P-(CH_2)_nPPh_2\}]$ has shown that in the solid state, the thiocyanate co-ordination changes from S_2 ($n = 1$) to SN ($n = 2$) and N_2 ($n = 3$). It is concluded that the bonding mode is controlled primarily by steric effects.^{189c}

¹⁸⁶ (a) A. Modinos and P. Woodward, *J.C.S. Dalton*, 1975, 1516; (b) D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, and J. S. Miller, *J. Amer. Chem. Soc.*, 1975, **97**, 1961.

¹⁸⁷ F. C. Seufftler and W. E. Geiger, *J. Amer. Chem. Soc.*, 1975, **97**, 5018.

¹⁸⁸ (a) T. McLeod, Lj. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, and R. Walker, *J. Organometallic Chem.*, 1975, **97**, C7; (b) W. J. Cherwinski, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Dalton*, 1975, 1156; (c) K. R. Dixon, K. L. Moss, and M. A. R. Smith, *ibid.*, p. 990. (d) P. L. Goggin, R. J. Goodfellow, and S. R. Haddock, *J.C.S. Chem. Comm.*, 1975, 176; (e) A. A. Kiffer, C. Masters, and J. P. Visser, *J.C.S. Dalton*, 1975, 1311.

¹⁸⁹ (a) S. J. Anderson and R. J. Goodfellow, *J.C.S. Chem. Comm.*, 1975, 443; (b) A. J. Carty and S. E. Jacobson, *ibid.*, p. 175; (c) G. J. Palenik, M. Mathew, W. L. Stiffen, and G. Berau, *J. Amer. Chem. Soc.*, 1975, **97**, 1059.

Hydrocarbon Activation.—Important in the search for a catalyst for activation of saturated hydrocarbons is the observation of hydrogen–deuterium exchange in alkanes, catalysed by platinum complexes.^{190a} Further work has shown that by use of H_2PtCl_6 in aqueous trifluoroacetic acid at 120°C , benzene has been oxidized to chlorobenzene and hexane to chlorohexanes.^{190b} Hydrogen–deuterium exchange at alkyl groups of L_2 moieties occurs in the complexes $[\text{Pt}_2\text{Cl}_4\text{L}_2]$ ($\text{L} = \text{PPr}_3$, PBu_3 , PBu^iPr_2 , PBu^tPr , PPrPh_2 , PPr_2Ph , or PBu^iPh_2) in aqueous (D_2O) acetic acid (CH_3COOD) medium. Exchange also occurs at the saturated (C-5) carbon of $\text{RCMe}_2\text{CH}=\text{CH}_2$ ($\text{R} = \text{Et}$, Pr , or Bu) under similar conditions. It may occur through dimeric complexes of the type $[\text{Pt}_2\text{Cl}_4(\text{RCMe}_2\text{CH}=\text{CH}_2)]$, isolated from the reaction medium, or related dimeric compounds.¹⁹¹

Diazeno Ligands.—Understanding of the properties of diazeno (N_2R) ligands has progressed from study of their platinum complexes. The bridging diazenido-ligand N_2H occurs in the complexes $[\text{Pt}(\text{N}_2\text{H})_2(\text{PR}_3)_2]_2^{2+}$ [$\text{PR}_3 = \text{PPh}_3$, PPh_2Me , or $\text{P}(\text{C}_6\text{H}_4\text{Me})_3$],¹⁹² prepared by hydrazine reduction of $\text{cis-}[\text{PtCl}_2(\text{PR}_3)_2]$. In the complex $[\text{PtCl}(\text{N}_2\text{C}_6\text{H}_4\text{F})(\text{PEt}_3)_2]$ the diazenido-group has the ‘doubly-bent’ struc-

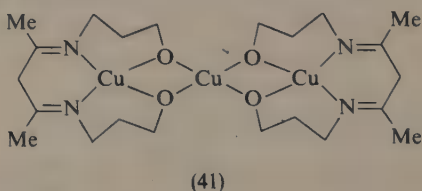
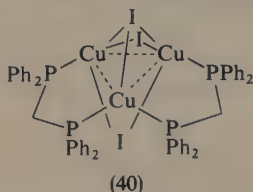
ture —N—N— and is readily protonated at both nitrogen atoms.¹⁹³

7 Group IB: Copper, Silver, and Gold

Principal activity this year has involved study of structural and magnetic properties of polynuclear complexes, and biologically relevant copper complexes.

Structural and Magnetic Studies.—The tetrameric species $[\text{MXPEt}_3]_4$ ($\text{M} = \text{Cu}$ or Ag ; $\text{X} = \text{Cl}$, Br , or I) have a distorted ‘cubane’ structure with μ_3 -halide bridges. Only for large halogens (Br or I) together with bulky phosphines (PPh_3) does the structure change to ‘step-like’. The complex $[(\text{CuI})_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ has a triangle of copper atoms connected by iodide and diphosphine bridges (40).¹⁹⁴

Polynuclear copper complexes, bridged by a variety of groups, show magnetic interaction of the antiferromagnetic type, and a number of further examples have been investigated this year. An unusual example is the trinuclear complex (41), the first example of a linear array of three oxygen-bridged copper(II) atoms. Magnetic



¹⁹⁰ (a) M. B. Tyrbine, A. E. Shilov, and A. A. Shteinman, *Doklady Akad. Nauk S.S.S.R.*, 1971, **198**, 380; R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc. (A)*, 1971, 3230; (b) J. R. Sanders, D. E. Webster, and P. B. Wells, *J. C. S. Dalton*, 1975, 1191.

¹⁹¹ A. A. Kiffen, C. Masters, and L. Raymond, *J.C.S. Dalton*, 1975, 853; P. A. Kramer and C. Masters, *ibid.*, p. 849.

¹⁹² M. Kember, S. Cenini, F. Conti, and R. Ugo, *J.C.S. Dalton*, 1975, 1081.

¹⁹³ S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 636; S. Krogsgund and J. A. Ibers, *ibid.*, p. 2298.

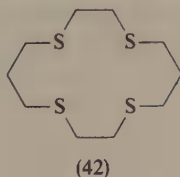
¹⁹⁴ M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1975, **14**, 2402; with S. J. Merdack *ibid.*, pp. 2041, 2496.

studies show that only two of the three electrons of the trimer are paired, only the spin-doublet state being populated.¹⁹⁵

Antiferromagnetic behaviour has been studied in the complexes diquinoline tetra- μ -trifluoroacetate(*O,O*)-dicopper(II),¹⁹⁶ $[\text{Cu}(\text{tren})_2\text{X}_2]^{2+}$ ($\text{tren} = 2,2',2''$ -triiminotriethylamine, $\text{X} = \text{Cl}$, NCO , or NCS),¹⁹⁷ $[\{\text{CuL}_2\text{X}_2\}_n]$ ($\text{X} = \text{Cl}$ or Br , $\text{L} =$ nicotinamide or isonicotinamide),¹⁹⁸ and bis(nicotinato)silver(II).¹⁹⁹ A correlation between metal environment and antiferromagnetic interaction in oxygen-bridged copper(II) dimers has been demonstrated²⁰⁰ and the magnetic properties of ternary oxides of copper in oxidation states (I) to (IV) have been investigated.²⁰¹

Unusual Valence States and Biologically Related Complexes.—A mixed-valence cluster compound $[\text{Cu}_4(\text{S}_2\text{CNEt}_2)_2\text{Cl}_4]$ consists of elongated square-pyramidal Cu^{II} linked by chloride and sulphur bridges to a tetrahedral Cu^{I} unit. It is formed by reduction of polynuclear, chloride-bridged $[\text{Cu}_2(\text{S}_2\text{CNEt}_2)_2\text{Cl}_2]$ and is associated with $[\text{Cu}_2(\text{S}_2\text{NEt}_2)_2\text{Cl}_2]$ dimers in the crystal.²⁰² The mixed $\text{Au}^{\text{III}}\text{--Au}^{\text{I}}$ compounds $[\text{Au}(\text{mnt})][\text{Au}(\text{MPh}_3)_2]$ ($\text{mnt} =$ maleonitrile dithiolate, $\text{M} = \text{P}$ or As) are converted into the Au^{II} anion, $[\text{Au}(\text{mnt})_2]^{2-}$, on treatment with $\text{Na}_2(\text{mnt})$, probably by an electron-transfer mechanism.²⁰³ A Cu^{III} complex, $[\text{Cu}(\text{G}_4)]^-$ ($\text{G}_4^{4-} =$ deprotonated tetraglycine), is unusual in that it is reasonably stable in aqueous solution, in contrast to the few other examples of Cu^{III} complexes. The $\text{Cu}^{\text{III}}\text{--Cu}^{\text{II}}$ potential, 0.140 V, is low enough to suggest that further similar compounds should be obtainable. $[\text{Cu}(\text{G}_4)]^-$ is formed by reaction of dioxygen with Cu^{II} tetraglycine complex, provided that photochemical inhibition of the reaction is avoided. It is suggested that $\text{Cu}^{\text{I}}\text{--Cu}^{\text{III}}$ couples could occur in biological systems such as galactose oxidase, thus avoiding high-energy free-radical intermediates.²⁰⁴

Study of copper-sulphur interactions in relation to copper-containing proteins such as oxidases has been an active field this year. The results of an X-ray photoelectron spectroscopic study of bean plastocyanin has been interpreted in terms of delocalized $\text{Cu}^{\text{II}}\text{--cysteine-sulphur}$ binding.²⁰⁵ Comparison has been made between copper-sulphur binding in various complexes and the environment of copper in



¹⁹⁵ W. A. Baker and F. T. Helm, *J. Amer. Chem. Soc.*, 1975, **97**, 2295, references therein.

¹⁹⁶ J. A. Moneland and R. J. Doedens, *J. Amer. Chem. Soc.*, 1975, **97**, 508.

¹⁹⁷ E. J. Laskowski, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 2449.

¹⁹⁸ R. P. Eckberg and W. E. Hatfield, *J.C.S. Dalton*, 1975, 1364.

¹⁹⁹ R. P. Eckberg and W. E. Hatfield, *Inorg. Chem.*, 1975, **14**, 1205.

²⁰⁰ E. Sinn, *J.C.S. Chem. Comm.*, 1975, 665.

²⁰¹ M. Arjomand and D. J. Machin, *J.C.S. Dalton*, 1975, **14**, 1205.

²⁰² A. R. Hendrickson, R. C. Martin, and D. Taylor, *J.C.S. Chem. Comm.*, 1975, 843.

²⁰³ T. J. Bergendahl and J. H. Waters, *Inorg. Chem.*, 1975, **14**, 2556.

²⁰⁴ F. P. Bossu, G. L. Burce, K. L. Chellappa, and D. W. Margerum, *J. Amer. Chem. Soc.*, 1975, **97**, 6896; G. L. Burce, D. W. Margerum, and E. B. Paningo, *J.C.S. Chem. Comm.*, 1975, 261.

²⁰⁵ P. J. Clendening, H. B. Gray, F. J. Grunthaner, and E. I. Solomon, *J. Amer. Chem. Soc.*, 1975, **97**, 3878.

'blue' proteins as is shown by its spectral parameters. In [bis-(2-pyridyl)disulphide]copper(I) perchlorate, the copper selects N_3S co-ordination, possibly its environment in natural systems.²⁰⁶ A dinuclear complex of copper(II) with oxidized glutathione is considered to be dimeric with Cu^{II} bridged by a disulphide unit. The Cu^{II} atoms interact, as shown by e.s.r. measurements, and the compound provides the basis for a scheme to account for the properties of the Cu pair in 'blue' oxidases which accepts two electrons.²⁰⁷ Copper complexes of cyclic or linear poly-thioethers show an absorption (600 nm) similar to that of 'blue' proteins, assigned in both complexes and proteins to an $S \rightarrow Cu^{II}$ charge-transfer band. Of this group, the complex of the ligand (42) has a planar arrangement about copper, suggesting that distorted symmetry about copper need not occur in the proteins. A further extrapolation from this work is that thioether sulphurs of methionine groups could be the copper-binding site of 'blue' proteins.²⁰⁸ The e.s.r. and visible spectra of a Cu^{II} α -mercaptopropionylglycine complex are similar to the corresponding parameters for 'blue' proteins.²⁰⁹ A kinetic study of the reduction of 'blue' proteins by $[Fe(edta)]^{2-}$ has been discussed in terms of an outer-sphere mechanism for all such proteins but laccase, which requires a specific protein activation to accept reductant.²¹⁰

In other studies of biological relevance, comparison of e.s.r. and electronic spectra of Cu^{II} carboxypeptidase A and model Cu^{II} complexes suggests a protein co-ordination significantly distorted from planar to tetrahedral symmetry.²¹¹ Other ligands of the amino-acid type whose interactions with copper have been studied include acetylhistamine, acetylhistidine [with Cu^I]; L-histidine, glycyglycine, and D-penicillamine, histidine peptides, simple dipeptides, epinephrine, L-3,4-dihydroxyphenylalanine and other catechols [with Cu^{II}].²¹² Steric and electronic effects in copper Schiff-base complexes have been reviewed.²¹³

Interaction of hydrazines and triazenes with copper have been studied. 1,1-Dimethylhydrazine reacts with copper(II) chloride to give a purple complex of 1,1-dimethyldiazene, $[Cu_2Cl_3\{Me_2N=N\}_2]$. Copper(II) bromide gives the salt $[Cu_2Br_3][Me_2N_2CHNMe_2]$, in which the central carbon of the cation appears to be derived from formaldehyde formed by hydrolysis of 1,1-dimethyldiazene.²¹⁴ The metal-metal bonded compounds $[L_2(CO)MCu(RNNNR)X]$ ($M = Rh^I$ or Ir^I ; $L = AsR_3$ or PR_3 ; $R = Me$ or aryl; and $X = Cl, Br, \text{ or } I$) have been prepared, and contain an $M^I \rightarrow Cu^I$ donor bond, bridged by the triazenido group.²¹⁵

²⁰⁶ M. M. Kadooka, L. G. Warner, and K. Seff, *J.C.S. Chem. Comm.*, 1975, 990, and references therein.

²⁰⁷ P. Kroneck, *J. Amer. Chem. Soc.*, 1975, **97**, 3840.

²⁰⁸ T. E. Jones, D. B. Rorabacker, and L. A. Schrymowycz, *J. Amer. Chem. Soc.*, 1975, **97**, 7485; L. C. Zimmer and L. L. Diaddario, *ibid.*, 7163, and references therein.

²⁰⁹ V. Sugiura, Y. Hirayama, H. Tamaka, and K. Ishizu, *J. Amer. Chem. Soc.*, 1975, **97**, 5577.

²¹⁰ S. Wherland, R. A. Holmerda, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 5260.

²¹¹ R. C. Rosenberg, C. A. Rost, P. K. Bernstein, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 2092.

²¹² P. A. Terinissi and A. Vitagliano, *J. Amer. Chem. Soc.*, 1975, **97**, 1572; S. H. Laurie, T. Lund, and J. B. Brynor, *J.C.S. Dalton*, 1975, 1389; R. P. Agarwal and D. D. Perrin, *ibid.*, p. 268; G. Brookes and L. D. Pettit, *ibid.*, p. 2302; R. K. Boggess and R. B. Martin, *J. Amer. Chem. Soc.*, 1975, **97**, 3076.

²¹³ H. S. Moslea and T. N. Waters, *Coordination Chem. Rev.*, 1975, **17**, 137.

²¹⁴ J. R. Boehm, A. L. Balch, K. F. Bizot, and J. H. Enemark, *J. Amer. Chem. Soc.*, 1975, **97**, 501.

²¹⁵ J. Kyper, P. I. Van Vliet, and K. Vrieze, *J. Organometallic Chem.*, 1975, **96**, 289.

8 Organometallic Compounds

By D. J. CARDIN

Department of Chemistry, Trinity College, Dublin University, Dublin 2

K. R. DIXON

Department of Chemistry, University of Victoria, Victoria, B.C., Canada

1 Introduction

This chapter deals first with main-group and early transition-metal (Groups III—VI) compounds (D.J.C.) followed by metal carbonyls and the later transition-metal derivatives (K.R.D.). The first part contains a section of shorter topics which were felt to be of wide general interest (in which the order of presentation is by the Group of the periodic table to which the appropriate metal belongs) and a selection of review articles and books.

In the main, the coverage is for the year 1975, but the second part covers specifically November 1974 to early November 1975.

2 Reactions of Metal Atoms

Conceptually one of the simplest and most attractive methods for the synthesis of organometallic compounds is the direct reaction of metal atoms with appropriate ligands (see Chapter 6, p. 120). This subject has received much attention recently, and various aspects have been reviewed by Skell,^{1a} Timms,^{1b} Koerner von Gustorf,² and Klabunde³ (for matrix-isolation work with metal carbonyls see Section 20). At present, all the transition metals can be used in this type of synthesis, many in gram quantities. Sandwich complexes have been made for chromium,⁴⁻⁶ titanium,⁷ and even tungsten.^{4b} The use of halogen-substituted arenes leads to some unexpected effects.^{3,8a} Thus for vanadium, whereas monosubstitution by chloro-, fluoro-, or trifluoromethyl-groups gives greater yields than with non-substituted benzene, disubstitution by the same groups gives reduced or zero yields. Yields were not so

¹ (a) P. S. Skell and M. J. McGlinchey, *Angew. Chem. Internat. Edn.*, 1975, **14**, 195; (b) P. L. Timms, *ibid.*, p. 273.

² E. A. Koerner von Gustorf, O. Jaenicke, O. Wolfbeis, and C. R. Eady, *Angew. Chem. Internat. Edn.*, 1975, **14**, 278.

³ K. J. Klabunde, *Angew. Chem. Internat. Edn.*, 1975, **14**, 287.

⁴ (a) P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Amer. Chem. Soc.*, 1973, **95**, 3337; (b) M. P. Silvon, E. M. Van Dam, and P. S. Skell, *ibid.*, 1974, **96**, 1945; (c) P. S. Skell and L. K. Wolf, *ibid.*, 1972, **94**, 7919.

⁵ R. Middleton, J. R. Hull, S. K. Simpson, C. H. Tomlinson, and P. L. Timms, *J.C.S. Dalton*, 1973, 120.

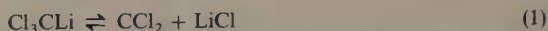
⁶ V. Graves and J. J. Lagowski, Abstracts, 165th A.C.S. Meeting, Dallas, Texas, 1973 (Paper No. INOR 52).

⁷ F. W. J. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J.C.S. Chem. Comm.* 1973, 866.

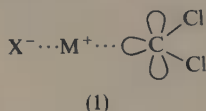
⁸ (a) K. J. Klabunde and H. F. Efnier, *J. Fluorine Chem.*, 1974, **4**, 115; (b) K. J. Klabunde and H. F. Efnier, *Inorg. Chem.*, 1975, **14**, 789.

sensitive with chromium, and the bis(trifluoromethyl)benzenechromium(0) complexes are remarkably air stable.^{8b} Interest also continues in the reactions of the vapours of main-group metals with organic molecules. Lithium vapour is known to react with chlorocarbons^{9a} and with carbon vapour,^{9b} giving polyolithio-organic compounds. The reaction of excess lithium vapour with alkenes has been studied and the products characterized by hydrolysis (H₂O and D₂O), affording alkenes and alkanes identified by n.m.r., g.l.c., and mass spectrometry, or by conversion into poly(trimethylsilyl) derivatives. Poly-lithioalkenes predominate in the products, and addition across the double bonds is relatively uncommon.^{9c} Although the reactions of aluminium vapour with olefins afforded no isolable aluminium species,^{4c} D₂O hydrolysis products were interpreted in terms of intermediate σ -bonded alkylaluminiums. More recently, the reaction with ethylene has provided evidence of a complex involving donation from the π -orbitals of the olefin, based on e.s.r. spectra of the matrix-isolated complex.¹⁰ Complexes are also formed with gallium and indium atoms.

The equilibrium between the carbene and 'carbenoid' species produced by reaction of lithium atoms with carbon tetrachloride is known to lie well to the left of

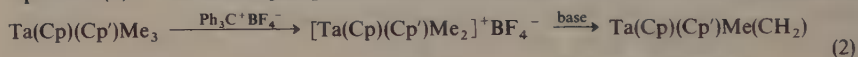


equation (1).^{11a} Careful analysis of i.r. data of the matrix products with the metals ⁶Li, Na, K, or Cs has revealed a further type of carbenoid species (1).^{11b}



3 Carbene and Carbyne Complexes

In spite of the preparation of numerous carbene complexes of the transition metals,¹² until recently no methylene complexes had been obtained, although they had been postulated as reaction intermediates^{13a-c} and complexes of secondary carbenes (CHR) are well known.^{13d,e} The synthesis of the first methylene complex is shown in equation (2).^{14a} The bis(cyclopentadienyl)methylene complex decomposes slowly in



Cp = $\eta^5\text{-C}_5\text{H}_5$; Cp' = $\eta^5\text{-C}_5\text{H}_4\text{R}$, R = H or Me; base = $\text{M}\ddot{\text{e}}_3\text{PCH}_2$, LiN(SiMe₃)₂, or NaOMe

⁹ (a) C. Chung and R. J. Lagow, *J.C.S. Chem. Comm.*, 1972, 1078; (b) L. A. Shimp and R. J. Lagow, *J. Amer. Chem. Soc.*, 1973, **95**, 1343; (c) J. A. Morrison, C. Chung, and R. J. Lagow, *ibid.*, 1975, **97**, 5015.

¹⁰ P. H. Kasai and D. McLeod, *J. Amer. Chem. Soc.*, 1975, **97**, 5607.

¹¹ (a) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, 1965, **87**, 4147, and refs. therein; (b) D. A. Hatzebuhler, L. Andrews, and F. A. Casey, *ibid.*, 1975, **97**, 187.

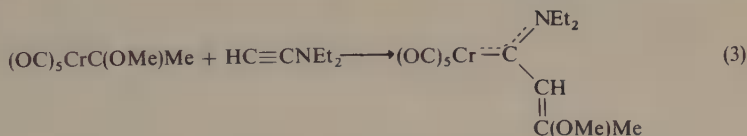
¹² D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99; M. F. Lappert, *J. Organometallic Chem.*, 1975, **100**, 139.

¹³ (a) M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. (A)*, 1967, 1508; (b) M. R. Collier, B. M. Kingston, and M. F. Lappert, *Chem. Comm.*, 1970, 1498; (c) N. J. Cooper and M. L. H. Green, *J.C.S. Chem. Comm.*, 1974, 761; (d) B. Çetinkaya, M. F. Lappert, G. M. McLaughlin, and K. Turner, *J.C.S. Dalton*, 1974, 1591; (e) R. R. Schrock, *J. Amer. Chem. Soc.*, 1974, **96**, 6796.

¹⁴ (a) R. R. Schrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6577; (b) L. J. Guggenberger and R. R. Schrock, *ibid.*, p. 6578; (c) L. J. Guggenberger and R. R. Schrock, *ibid.*, p. 2935.

deuteriobenzene solution, forming 0.5 mol of $\text{Ta}(\text{Cp})_2\text{Me}(\text{CH}_2\text{CH}_2)$ and presumably $\text{Ta}(\text{Cp})_2\text{Me}$, which can be trapped as $\text{Ta}(\text{Cp})_2\text{Me}(\text{CO})$ under carbon monoxide. With CD_3I , the methylene complex yields CH_3D and the two isomers of $\text{Ta}(\text{Cp})_2(\text{CH}_2\text{CD}_2)\text{I}$, presumably *via* $\text{Ta}(\text{Cp})_2\text{Me}(\text{CH}_2\text{CD}_3)\text{I}$. This, and other reactions show nucleophilic properties for the *co-ordinated* methylene group. The crystal structure of the complex reveals two eclipsed cyclopentadienyl rings related by a mirror plane containing the $\text{C}-\text{Ta}-\text{C}$ bonds of the $\text{CH}_2-\text{Ta}-\text{CH}_3$ system.^{14b} By contrast with the majority of carbene complexes,¹² the methylene group can π -bond only with the metal atom, and the $\text{Ta}-\text{CH}_2$ distance [2.206(10) Å] is considerably shorter than the $\text{Ta}-\text{CH}_3$ (*ca.* 2.25 Å) of the same compound, but longer than the formal triple bond [1.76(2) Å] of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{CCMe}_3\text{Li}(\text{NN}'\text{-dimethylpiperazine})$.^{14c} This π -bonding is supported for the cyclopentadienyl(methylcyclopentadienyl)methylene analogue, for which n.m.r. measurements indicate a rotational barrier about the $\text{Ta}-\text{CH}_2$ bond in excess of 21 kcal mol⁻¹.

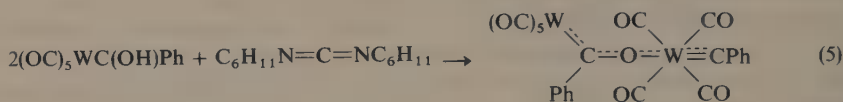
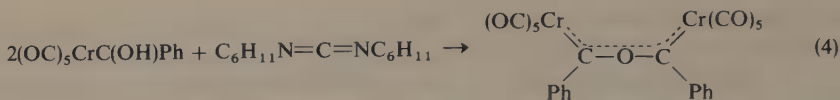
Insertion reactions into $\text{M}-\text{C}_{\text{carb}}$ bonds are not common, and few have been reported since the curious reaction of PhSeH with carbenes of the Group VIA metals was reported.^{15a} The insertion of aminoacetylenes, equation (3), has now been described.^{15b}



Carbyne complexes, which were originally prepared from carbene species using boron halides^{15c} have now been obtained by a variety of routes. {A number of *C*-chlorocarbene complexes, such as $[\text{Cr}(\text{CO})_5(\text{CCINMe}_2)]$, $[\text{Mn}(\text{CO})_5-(\text{CCINMe}_2)]^+$, or $[\text{Rh}(\text{CO})\text{Cl}(\text{CCINMe}_2)]$, which may be intermediates in the carbyne synthesis, have been prepared from $(\text{Me}_2\text{NCCl}_2)^+\text{Cl}^-$ and $\text{Na}^+_2[\text{Cr}(\text{CO})_5]^{2-}$, $\text{Na}^+[\text{Mn}(\text{CO})_5]^-$, or Rh^1 species.^{15d}}. Thus, whereas chromium carbenes with hydroxyl substituents react with carbodi-imide forming new carbene complexes [equation (4)],^{15e} tungsten analogues give dinuclear carbyne derivatives [equation (5)]. Whereas it has been known for some time that electron-rich olefins, such as $[:\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}]_2$, are sources of metal carbene complexes,¹² it has now been shown that under milder conditions this olefin and $[\text{Cr}(\text{CO})_4(\text{norbornadiene})]$ give the N,N-bonded $[\text{Cr}(\text{CO})_4(\text{olefin})]$ complex.^{15f}

The effect on structure and bonding of heteroatom substituents on the C_{carb} atom of carbene complexes has been well documented, but corresponding information on

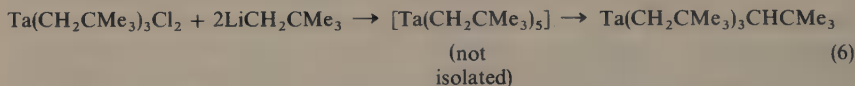
¹⁵ (a) E. O. Fischer and V. Kiener, *Angew. Chem. Internat. Edn.*, 1967, **6**, 961; (b) K. H. Dötz and C. G. Kreiter, *J. Organometallic Chem.*, 1975, **99**, 309; (c) E. O. Fischer, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorenz, *Angew. Chem. Internat. Edn.*, 1973, **12**, 564; (d) A. J. Hartshorn, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1975, 929; (e) E. O. Fischer, K. Weiss, and C. G. Kreiter, *Chem. Ber.*, 1975, **107**, 3554; (f) B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Chem. Comm.*, 1975, 683; (g) E. O. Fischer, G. Kreis, F. R. Kreissl, W. Kalbfus, and E. Winkler, *J. Organometallic Chem.*, 1974, **65**, 113; (h) E. O. Fischer, G. Huttner, W. Kleine, and A. Frank, *Angew. Chem. Internat. Edn.*, 1975, **14**, 760; (i) E. O. Fischer and V. Schubert, *J. Organometallic Chem.*, 1975, **100**, 59.



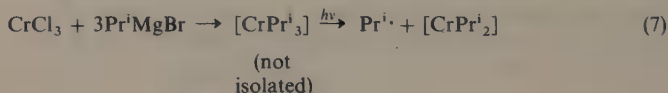
carbyne derivatives is new. Diethylaminocarbyne complexes of tungsten^{15g} and chromium have been obtained, and the crystal structure of the latter has been reported.^{15h} While the $\text{Cr}\equiv\text{C}$ distance of *trans*- $[\text{Et}_2\text{NC}\equiv\text{Cr}(\text{Br})(\text{CO})_4]$ [1.720(10) Å] is not significantly greater than that found in the analogous methylcarbyne complex,¹⁵ⁱ the $\text{C}\cdots\text{N}$ distance [1.294(12) Å] is indicative of considerable double-bond character.

4 α - and β -Eliminations

Of the various elimination processes involved in the decomposition of metal alkyls, the α -process is relatively little documented and was not established for homoleptic derivatives of the early transition elements.^{16a} However, evidence had been obtained for such a mechanism occurring in tungsten alkyls,^{13c} supported by D-labelling experiments. The α -abstraction process has now also been demonstrated in a homoleptic species [equation (6)], also supported by labelling studies.^{16b}



It appears from data so far available^{14a} that intramolecular α -abstraction will occur most easily when the metal atom is sterically crowded. The isolation of stable Pr_4^iCr shows that neither this last impression, nor the view that alkyls with β -hydrogen atoms will be unstable, has general validity. The mechanism proposed^{16c} [equations (7) and (8)] was suggested by the increase of yield observed upon irradiation. Analogous compounds replacing isopropyl with methyl, ethyl, or *t*-butyl



groups could not be obtained, and the stability of the isopropyl species was attributed to the stability of the radicals as well as to steric crowding.

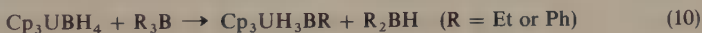
¹⁶ (a) P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209; (b) R. R. Schrock, *J. Amer. Chem. Soc.*, 1974, **96**, 6796; (c) J. Müller and W. Holzinger, *Angew. Chem. Internat. Edn.*, 1975, **14**, 760.

5 Organo-lanthanides and -actinides

An area which attracted much attention during 1975 is that of organo-lanthanide and -actinide species. Several review articles appeared,^{17a-d} and a number of interesting publications will be described. The allyl compounds $\text{Cp}_2\text{MC}_3\text{H}_5$ appear to be π -bonded when M is a lanthanide (Sm, Er, or Ho),^{17e} whereas a crystal structure of $\text{Cp}_3\text{UCH}_2\text{C}(\text{Me})\text{CH}_2$ shows that the 2-methylallyl group is σ -bonded;^{17f} σ -bonding had previously been suggested for the allyl analogue^{17g} on the basis of i.r. spectroscopy, and indeed the new lanthanide species show a band at 1533 cm^{-1} associated with the C—C stretching mode of π -allyl groups. The organometallic chemistry of the lanthanides has been mainly restricted to π -bonding ligands,^{17h,j} but alkyl and aryl derivatives have now been prepared by the organolithium route for Gd, Er, and Yb [equation (9)]. Although air- and moisture-sensitive, the new



compounds show thermal stability, decomposing only above 130°C under Ar.^{17k} The unusual temperature dependence of magnetic susceptibility might provide evidence for considerable covalency in the new species, and is not observed, for example, in the π -bonded complexes. The reaction of trimethylsilylmethyl-lithium with uranium tetrachloride afforded solvates of $\text{Li}_2\text{U}(\text{CH}_2\text{SiMe}_3)_6$, the first uranium compound with more than a single metal-carbon σ -bond.^{17l} Vibrational spectra of the product of the exchange reaction shown in equation (10) indicate a triple hydrogen bridge. The ^{11}B decoupled ^1H n.m.r. spectrum of Cp_3UBH_4 exhibits, at



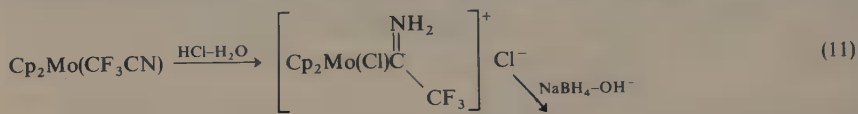
low temperatures, collapse of the BH_4 multiplet, although the slow exchange limit could not be reached.^{17m} This is the first time for any metal borohydride species that slowing of the bridge/terminal hydrogen rearrangement could be observed. Bis(cyclo-octatetraenyl)uranium and related molecules are highly air-sensitive. An air-stable 'uranocene' derivative has been obtained by using 1,3,5,7-tetraphenylcyclo-octatetraene dianion and uranium tetrachloride.¹⁷ⁿ The stability is presumably the result of steric blocking of the metal atom, and consequently suggests that oxidative attack (O_2) takes place at U, and not at the ring.

6 Cyclopentadienyl and Cyclo-octatetraenyl Compounds

Current interest in the bis(cyclopentadienyl)metal derivatives of the Group VIA metals undoubtedly springs from the discovery of the remarkable reactions with

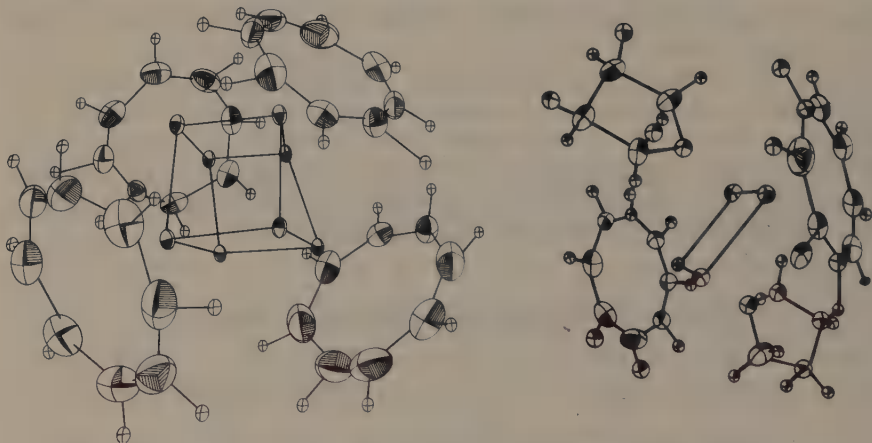
¹⁷ (a) M. Tsutsui, N. Ely, and A. E. Gebala, *Ann. New York Acad. Sci.*, 1974, **239**, 160; (b) M. Tsutsui, U.S. Ntis, AD-A Rep. 1975, No. 008871 [Govt. Report Announce. Index (U.S.), 1975, **75**, 63]; (c) T. J. Marks, *J. Organometallic Chem.*, 1975, **95**, 301; (d) N. S. Vyazankin, R. N. Shchelokov, and O. A. Kruglaya, *Metody Elem.-Org. Khim.*, 1974, **2**, 905 [Nauka, Moscow]; (e) M. Tsutsui and N. Ely, *J. Amer. Chem. Soc.*, 1975, **97**, 3551; (f) G. W. Halstead, E. C. Baker, and K. N. Raymond, *ibid.*, p. 3049; (g) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, 1967, **6**, 179, and refs. therein; (h) See for example, K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwieser, *J. Amer. Chem. Soc.*, 1973, **95**, 8650; (j) H. Gysling and M. Tsutsui, *Adv. Organometallic Chem.*, 1970, **9**, 361; (k) M. Tsutsui and N. M. Ely, *J. Amer. Chem. Soc.*, 1975, **97**, 1280; (l) R. Anderson, E. Carnowa-Guzman, K. Mertis, E. Sigurdson, and G. Wilkinson, *J. Organometallic Chem.*, 1975, **99**, C19; (m) T. J. Marks and J. R. Kolb, *J. Amer. Chem. Soc.*, 1975, **97**, 27; (n) A. Streitwieser and R. Walker, *J. Organometallic Chem.*, 1975, **97**, C41.

C—H bonds.^{18a} The Mo and W compounds are relatively reactive compared with the Cr, but only the W species inserts into aromatic C—H bonds. Reactivity with CO also varies, and the adduct $\text{Cp}_2\text{Cr}(\text{CO})$ is formed reversibly under carbon monoxide, in contrast to the known, stable Mo and W analogues.^{18b} Not surprisingly, the complexes $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_7)\text{M}(\text{CO})_2$ are stable for all three metals, but tungsten is unique in forming $\text{Cp}_2\text{W}(\text{CO})_2$, a 20-electron complex. The carbonyl i.r. stretches exhibit no variations attributable to 'back-bonding' effects, which are presumably not significant in determining reactivity differences. These are discussed subsequently in terms of structure and bonding.^{18c} New η^2 -nitrile complexes of molybdenocene have been obtained, some of which can be reduced to yield ammonia, *via* isolable iminium intermediates [equation (11)].^{18d} These adducts differ from earlier related



$\text{NH}_3 + \text{Cp}_2\text{MoH}_2 + \text{unidentified hydrocarbons}$

molecules, which either proved to be σ -bonded^{18e} or had labile nitrile molecules.^{18f} (Details of aza-allyl derivatives of Mo and W are described in Section 22.) The dicarbonyl derivative of titanocene is now more easily accessible,^{18g} and its crystal structure has been reported.^{18h} By contrast with titanocene dichloride, the cyclopentadienyl rings are eclipsed. The Ti—C(O) bond length [2.030(11) Å] is the first structural information available for a Group IVA metal carbonyl. Cyclo-octatetraene (cot) complexes of titanium have been prepared, by a new route, and



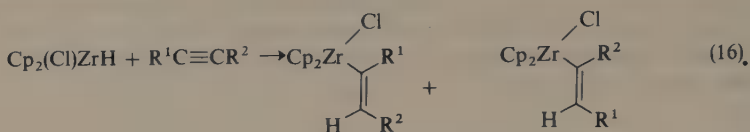
(Reproduced by permission from *J. Organometallic Chem.*, 1975, **92**, 329)

- ¹⁸ (a) K. Elmitt, M. L. H. Green, R. A. Forder, I. Jefferson, and K. Prout, *J.C.S. Chem. Comm.*, 1974, 747; (b) K. L. Tang Wong and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1975, **97**, 5143; (c) H. H. Brintzinger, L. L. Lohr, and K. L. Tang Wong, *ibid.*, p. 5146; (d) J. L. Thomas, *ibid.*, p. 5943; (e) J. G. Dunn and D. Edwards, *Chem. Comm.*, 1971, 482, and refs. therein; (f) W. J. Bland, R. D. W. Kemmitt, and R. D. Moore, *J.C.S. Dalton*, 1972, 1292; (g) H. Alt and M. D. Rausch, *J. Amer. Chem. Soc.*, 1974, **96**, 5936; (h) J. L. Atwood, K. Stone, H. G. Alt, D. C. Hrnir, and M. D. Rausch, *J. Organometallic Chem.*, 1975, **96**, C4; (j) H. R. Van der Wal, F. Overzet, H. O. Van Oven, J. L. de Boer, H. J. De Liefde-Meijer, and F. Jellinek, *J. Organometallic Chem.*, 1975, **92**, 329; (k) J. Knol, A. Westerhof, H. O. Van Oven, and H. J. De Liefde-Meijer, *J. Organometallic Chem.*, 1975, **96**, 257.

$$(\eta^8\text{-cot})(\eta^5\text{-Cp})\text{Ti} + \frac{1}{2}\text{I}_2 \rightarrow (\eta^8\text{-cot})(\eta^5\text{-Cp})\text{TiI} \quad (12)$$
$$\begin{array}{c}
 \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3 \\
 \text{or} \\
 + \quad \text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3 \\
 \text{or} \\
 \text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3
 \end{array}
 \rightarrow \text{Cp}_2(\text{Cl})\text{Zr}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad (14)$$
$$\text{Cp}_2(\text{Cl})\text{ZrCHDCHDBu}^t + \text{Br}_2 \xrightarrow{\text{benzene}} \text{BrCHDCHDBu}^t \quad (15)$$

¹⁹ (a) C. A. Bertelo and J. Schwartz, *J. Amer. Chem. Soc.*, 1975, **97**, 228; (b) G. Fachinetti and C. Floriani, *J. Organometallic Chem.*, 1974, **71**, C5; (c) G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1972, 654; (d) J. A. Labinger, D. W. Hart, W. E. Seibert, and J. Schwartz, *J. Amer. Chem. Soc.*, 1975, **97**, 3851; (e) P. L. Bock, D. J. Baschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *ibid.*, 1974, **96**, 2814; (f) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, 1971, **93**, 5283; (g) See G. M. Whitesides and D. J. Boschetto, *ibid.*, 1971, **93**, 1529; (h) D. W. Hart, T. F. Blackburn, and J. Schwartz, *ibid.*, 1975, **97**, 679.

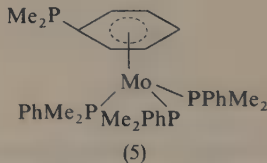
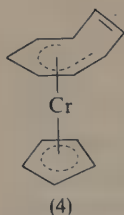
Zr—H bond of Cp_2ClZrH also occurs with disubstituted acetylenes. When unsymmetrical acetylenes are employed, a mixture of products is obtained initially [equation (16)], dependent on the bulk of the substituents.^{19h} The initial product mixture



slowly (at room temperature) rearranges to a composition of higher regioselectivity, a process catalysed by the initial zirconium hydride. Since pure vinylzirconium derivatives undergo no such rearrangement, whereas it is known to occur for the alkyls, the process is envisaged as taking place through the alkyl species $\text{ZrR}^1\text{CH}=\text{CHR}^2\text{Zr}$ formed by double hydrosilyration of the acetylene.

■ Sixteen-electron Compounds

It has often been remarked that in their organometallic compounds, the transition elements 'obey' the effective atomic number rule (especially in the middle of the series) with surprising frequency, sometimes adopting unexpected structures. Two recent examples are shown in (4)^{20a} and (5).^{20b} Perhaps more surprising are the



well-known pyrazolylborato-complexes of molybdenum. Sixteen-electron complexes of Mo or W were prepared from $\text{CpM}(\text{Cl})(\text{CO})_3$ and acetylenes RC_2R ($\text{R} = \text{Me}, \text{CF}_3$, or CO_2Me) in which the (three) carbonyl groups were displaced by two acetylene molecules.^{20c} The complex $[\text{Ph}_2\text{B}(\text{pz})_2](\text{CO})_2\text{MoC}_3\text{H}_4\text{Me}$, unlike related compounds,²¹ has η^3 -2-methylallyl, carbonyl, and pyrazolyl N-atoms as Mo ligands, without additional metal co-ordination, making it a 16-electron species.

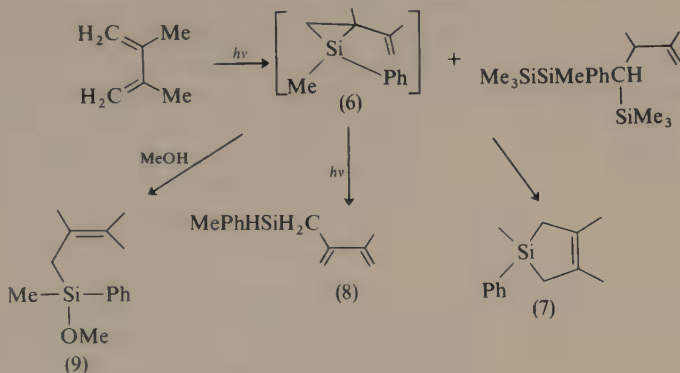
■ Silacyclopropanes

Silacyclopropanes have long been known as intermediates in thermolyses and photolyses of organosilicon compounds. For example, the photolysis of 2-phenylheptamethyltrisilane afforded a silacyclopropane which was trapped with

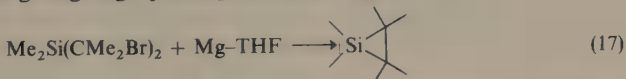
²⁰ (a) J. Müller and H. Menig, *J. Organometallic Chem.*, 1975, **96**, 83; (b) R. Mason, K. M. Thomas, and G. A. Heath, *J. Organometallic Chem.*, 1975, **90**, 195; (c) J. L. Davidson, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 706.

²¹ F. A. Cotton, T. LaCour, and A. G. Stannislowski, *J. Amer. Chem. Soc.*, 1974, **96**, 754.

methanol.^{22a,b} The products of photolysis of the same trisilane with dimethylbutadiene (Scheme 1) provide evidence for the formation of a 1,2-adduct (silacyclopropane), (6), which undergoes further rearrangement either to give (7), which could have resulted from direct 1,4 attack, or to give (8). The isolation of (8) is best



explained by further reaction of (6), whose existence is also supported by trapping with methanol after irradiation, affording (9).^{22c} The thermolysis of phenyltrimethylsilyldiazomethane, which affords a benzosilacyclopentene, had previously been reported to proceed *via* a silacyclopropane intermediate, but this route has now been ruled out, and it seems likely that the intermediates are the phenylcarbene and the cycloheptatrienylidene derived therefrom.^{22d} The first stable silacyclopropanes were isolated in 1972, and proved to be highly reactive compared with larger rings containing silicon.^{22e} Hexamethylsilacyclopropane has been synthesized [equation (17)], and is also stable under inert atmosphere, but reacts with the protic species H_2O , NH_3 , or alcohols giving ring-opened products having Si—O or Si—N bonds.^{22f}

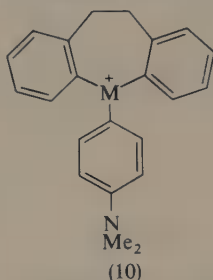


The new compound provides a low-temperature route to dimethylsilene. The latter has been identified by several techniques, including trapping by a number of silanes. The previously prepared silacyclopropanes did not afford silenes on thermolysis, but gave dimeric and polymeric species.^{22e,g} MO calculations on 7-siladispiro[2,0,2,1]heptane suggest increased Si—C bond strength due to hyperconjugative effects, and further, that *d*— σ -hyperconjugation may also contribute significantly to the strengthening of the Si—C bond in the (unknown) cyclopropylidenesilanes.^{22h} The tetraphenyl-substituted boracyclopropenyl anion has been proposed in reactions following the photolysis of sodium tetraphenylborate in the presence of tolan.^{22j}

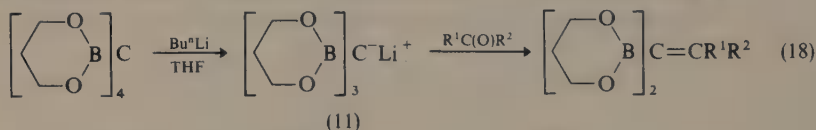
²² (a) M. Ishikawa, M. Ishigino, and M. Kumada, *J. Organometallic Chem.*, 1973, **49**, C71; (b) M. Ishikawa and M. Kumada, *ibid.*, 1974, **81**, C3; (c) M. Ishikawa, F. Ohi, and M. Kumada, *ibid.*, 1975, **85**, C23; (d) J. J. Barton, J. A. Kilgour, R. R. Gallici, A. J. Rothschild, J. Slutsky, A. D. Wolf, and M. Jones, *J. Amer. Chem. Soc.*, 1975, **97**, 658; (e) R. L. Labert and D. Seyferth, *ibid.*, 1972, **94**, 9246; (f) D. Seyferth and D. C. Annarelli, *ibid.*, 1975, **97**, 2273; (g) D. Seyferth and D. C. Annarelli, *ibid.*, 1975, **97**, 7162; (h) P. D. Mollere and K. Hoffman, *ibid.*, 1975, **97**, 3680; (j) J. J. Eisch, K. Tameo, and R. J. Wilcsek, *ibid.*, 1975, **97**, 895.

10 Main-group Organometallic Ions

Although siliconium ions (five-co-ordinate) have been described as intermediates, and attempts have been made to trap silicenium ions (three-co-ordinate), the existence of the latter had not been established prior to 1975. The ion (10; $M = Si$) has now been trapped following reaction between the silepin (10; $M = SiH$) and an equimolar quantity of triphenylcarbenium perchlorate in CH_2Cl_2 at *ca.* $-50^\circ C$.^{23a} The reaction produces a coloured solution which reacts with $NaBD_4$ -diglyme or $NaBH_4 \cdot H_2O$ -dioxan to yield the silepin ($Si-D$), or a mixture of this ($Si-H$) and the silanol, respectively. The substituted ferrocenylsilicenium ion has also been obtained.^{23b}



Another interesting group of organometallic ions consists of boron-substituted carbanions. These have been suggested as intermediates in a number of reactions, including the base-induced deboronation of *gem*-diboryl species, which has been employed in the synthesis of $C=C$ compounds from $C=O$ ones. The ion (11) [equation (18)] has been isolated and characterized (including n.m.r. data), and shown to react with a variety of carbonyl compounds affording substituted ethylenes.^{23c}



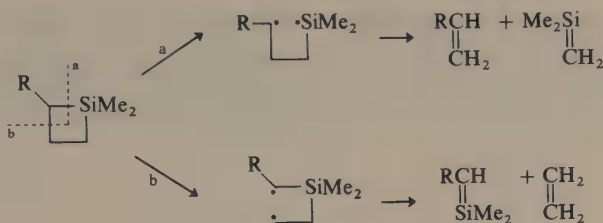
11 Double-bonded Silicon

The pyrolysis of silacyclobutanes and production of intermediates containing double bonds to silicon were reported by Gusel'nikov and colleagues in 1966,^{24a} and a short review of this area has now been published by the same group.^{24b} The subject continues to excite interest, concerning both the mechanistic details and reactivity and the identification of new $Si=E$ bonds. Two groups have reported studies on

²³ (a) J. Y. Corey, *J. Amer. Chem. Soc.*, 1975, **97**, 3237; (b) J. Y. Corey, D. Gust, and K. Mislow, *J. Organometallic Chem.*, 1975, **101**, C7; (c) D. S. Matteson and L. A. Magelee, *ibid.*, 1975, **93**, 21.

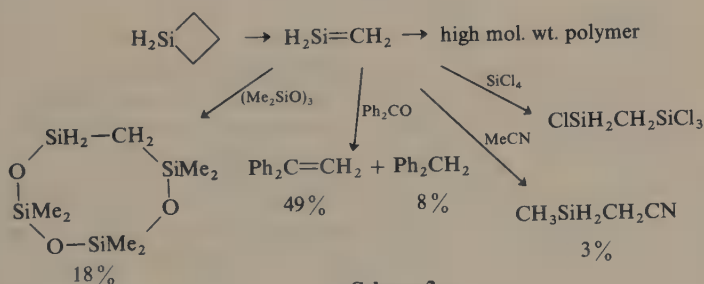
²⁴ (a) N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov, and V. I. Zav'yalov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1966, 589; (b) L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Accounts Chem. Res.*, 1975, **8**, 18; (c) T. J. Barton, G. Marquardt, and J. A. Kilgour, *J. Organometallic Chem.*, 1975, **85**, 317; (d) C. M. Golino, R. D. Bush, P. On, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1975, **97**, 1957; (e) C. M. Golino, R. D. Bush and L. H. Sommer, *ibid.*, 1975, **97**, 7371; (f) L. H. Sommer and J. McLick, *J. Organometallic Chem.*, 1975, **101**, 171; (g) Yu. A. Ustyynyuk, P. I. Zakharov, A. A. Azizov, G. A. Shchembelov, and I. P. Gloviovov, *ibid.*, 1975, **96**, 195.

thermolysis of 2-substituted 1,1-dimethylsilacyclobutanes and conclude that C—C rather than Si—C bond cleavage occurs.^{24c,d} The products from both cleavage mechanisms are shown in Scheme 2, and the predominance of products formed *via* path b shows C—C rupture, while the magnitude of the substituent effect makes the alternative (Si—C) bond breakage an unlikely initial step.^{24d}



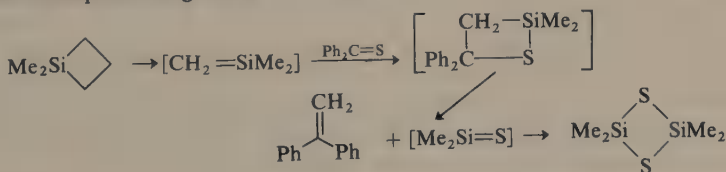
Scheme 2

The unsubstituted silaethene appears to be generated in the pyrolysis (560 °C, N₂ flow system) of silacyclobutane. It polymerizes in the absence of traps; reactions with a number of reagents are presented in Scheme 3.^{24e}



Scheme 3

Evidence for the first Si=S intermediate comes from the reaction of thiobenzophenone with pyrolysis products of 1,1-disubstituted silacyclobutanes, the proposed reaction sequence is given in Scheme 4.^{24f}



Scheme 4

No isolable Si=C species has yet been described, but the synthetic chemist is challenged by the suggestion, based on CNDO/2 calculations, that 6,6-dimethyl-6-silafulvene is potentially such a stable material.^{24g}

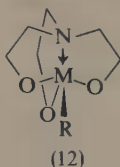
12 Silatranes and Stannatranes

The discovery of neurophysiological effects in tricyclic esters having the structure (12; M = Si) has provided impetus for further chemical studies. Numerous syntheses

of substituted derivatives of the silicon ('silatrane') compounds have been published,^{25a,b} as has a new route, equation (19) to the tin analogues ('stannatranes').^{25c} The tin compounds also have five-co-ordinate metal, although n.m.r. evidence has been interpreted in terms of equilibrium between four- and five-co-ordinate species in solution.^{25c}

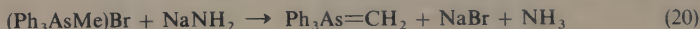


The acid-catalysed solvolysis of 1-organosilatrane has been studied. It is first-order in silatrane, and probably goes by initial protonation of the nitrogen, with breaking of the Si—N bond, but the protonation is almost complete at the transition state.^{25d}



13 Ylides

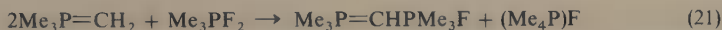
The chemistry of ylides in an inorganic context has been developed over the past few years, and the chemistry of P, As, and S ylides, and in particular the work of Schmidbaur's group, has been reviewed.^{26a} Relatively few arsonium ylides have been isolated, and the first example which is not stabilized by carbonyl groups was recently prepared [equation (20)].^{26b} This thermally unstable compound gives on



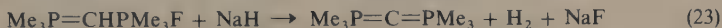
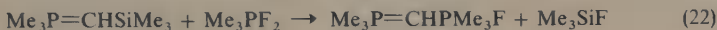
decomposition triphenylarsine, polymethylene, and ethylene among the products. The $^1\text{J}(\text{CH})$ coupling (compared with the arsonium cation) suggests that little rehybridization occurs on the $\text{CH}_3 \rightarrow \text{CH}_2$ change, *i.e.* that the carbon atom in the methyllide has pseudo-tetrahedral geometry. The same ylide has also been obtained using NaH , and found to react with a number of acyl halides with transylidation.^{26c,d} Interest in $[\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]^+\text{X}^-$, and in the di-ylide $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$, stemmed from the unusual physical properties: the PNP angle is dependent on the anion, and the ylide is triboluminescent probably as a result of a delicate balance of energy levels associated with the angular deformation. The methyl analogue can be prepared as shown in equations (21)—(23).^{26e} The di-ylide is a very air-sensitive material, a strong base, and a stronger nucleophile than mono-ylides.^{26e}

²⁵ (a) M. G. Voronkov, V. M. D'yakov, and L. I. Gubanova, *Zhur. obshchei Khim.*, 1975, **45**, 1901, 1902, 1903, 1904, 1905; (b) E. Popowski, M. Michalik, and H. Kelling, *J. Organometallic Chem.*, 1975, **88**, 157; (c) M. Zeldin and J. Ochs, *ibid.*, 1975, **86**, 369; (d) A. Daneshrad, C. Eaborn, R. Eidschinken, and D. R. M. Walton, *ibid.*, 1975, **90**, 139.

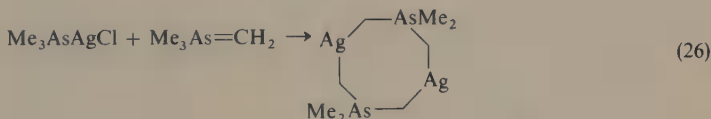
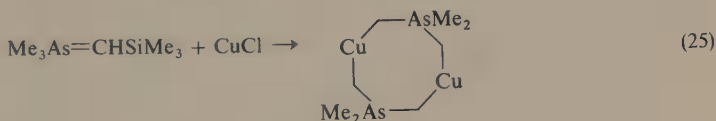
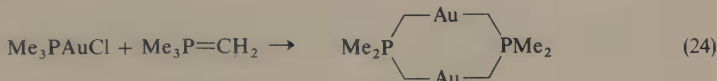
²⁶ (a) H. Schmidbaur, *Accounts Chem. Res.*, 1975, **8**, 62; (b) Y. Yamamoto and H. Schmidbaur, *J.C.S. Chem. Comm.*, 1975, 668; (c) P. S. Kendurkar and R. S. Tewari, *J. Organometallic Chem.*, 1975, **102**, 141; (d) P. S. Kendurkar and R. S. Tewari, *ibid.*, p. 173; (e) O. Gasser and H. Schmidbaur, *J. Amer. Chem. Soc.*, 1975, **97**, 6281; (f) H. Schmidbaur, H. J. Füller, and F. H. Kohler, *J. Organometallic Chem.*, 1975, **99**, 353; (g) H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, 1975, **13**, 85; (h) H. Schmidbaur and R. Wolfgang, *Chem. Ber.*, 1975, **108**, 2659; (j) E. Kurras, U. Rosenthal, H. Mennenger, G. Oehme, and G. Engelhardt, *Z. Chem.*, 1974, **14**, 160; (k) E. Kurras, H. Mennenger, G. Oehme, U. Rosenthal, and G. Engelhardt, *J. Organometallic Chem.*, 1975, **84**, C13.



or



Reaction of phosphorus ylides with trialkyl derivatives of Ga, In, or Tl, has been found to yield phosphonium betaine structures, *e.g.* $\text{Me}_3\text{P}^+-\text{CH}_2-\text{GaMe}_3$.^{26f} The use of ylides in the preparation of metal alkyls is well known. Recent examples are shown in equations (24)–(26), including extension to the relatively novel arsenic ylides.^{26g,h}



An interesting related reaction is the synthesis of homoleptic alkyls of chromium^{26j} and molybdenum^{26k} using phosphonium salts and alkyl metal anions [equation (27)]. The molybdenum species are less air-sensitive and reactive, and react with



acetic acid to give molybdenum(II) acetate. The probable structure involves bridging alkyl ligands in an arrangement similar to the acetate.

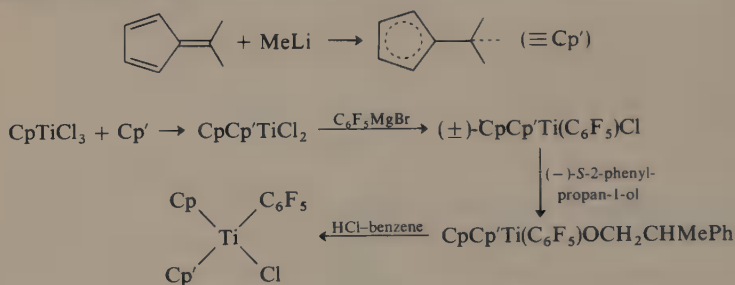
14 Chiral Metal Centres

The synthesis of organometallic compounds with chiral metal centres continues to receive attention, particularly for main-group elements. Many of the syntheses use classical methods involving separation of diastereomeric pairs, but the hydrosilylation of (–)-menthone or (+)-camphor using Wilkinson's catalyst or an analogue having optically active phosphine ligands has been reported.^{27a} The alkoxysilanes are obtained in up to 82% optical purity, and can be converted into alkyl silanes using

²⁷ (a) R. J. P. Corriu and J. J. E. Moreau, *J. Organometallic Chem.*, 1975, **91**, C27; (b) R. J. P. Corriu, F. Larcher, and G. Royl, *J. Organometallic Chem.*, 1975, **102**, C25; (c) J. Tirouflet, A. Dormond, J. C. Leblanc, and F. Le Moigne, *Tetrahedron Letters*, 1973, 257; (d) F. Le Moigne, A. Dormond, J. C. Leblanc, C. Moise, and J. Tirouflet, *J. Organometallic Chem.*, 1973, **54**, C13; (e) C. Moise, J. C. Leblanc, and J. Tirouflet, *J. Amer. Chem. Soc.*, 1975, **97**, 6272; (f) J. C. Leblanc, C. Moise, and T. Bounthakna, *Compt. rend.*, 1974, **278**, 973; (g) G. Simonneaux, A. Meyer, and G. Jaouen, *J.C.S. Chem. Comm.*, 1975, 69.

Grignard reagents with retention of configuration. The first optically active bifunctional silanes in which the Si atom is the only chiral centre, α -naphthylferrocenylfluorosilane and α -naphthylferrocenylchlorofluorosilane, have been prepared. Fluorine was introduced by reaction of mentoxysilanes with BF_3 , which goes with inversion of configuration; chlorine was attached with retention using PdCl_2 and silanes.^{27b}

Relatively few early transition-metal compounds with chirality at the metal have been reported, partly because the mechanism and steric course of reactions are not always straightforward, particularly at octahedral metals. Full details are now available of the first resolved titanocene derivative, of which preliminary reports have appeared.^{27c,d} The preparation is outlined in Scheme 5,^{27e} and is based on the separation of diastereoisomers. The second chiral centre was removed by HCl cleavage, which has been established^{27f} to be selective and stereospecific.



Scheme 5

The first optically active chromium(0) species enantiomeric at Cr have been prepared from optically pure 1-S-[1-CO₂Me-2-Me-(η^6 -C₆H₄)]Cr(CO)₃ by substitution of carbonyl by CS and (PhO)₃P, followed by removal of the initial chirality by reduction with $\text{LiAlH}_4\text{-AlCl}_3$. The preparation of chiral arenechromium tricarbonyls offers the possibility of catalytic asymmetric syntheses.^{27g}

15 Metal-Carbon Bond Strength Data

Thermochemical data on alkyl and aryl derivatives of transition metals, and derived strengths of M—C bonds do not, in general, support the once widely held view that such bonds are weak and can only be sustained by suitable ligand combinations. Mean bond-energy terms for the bonds M—C in homoleptic metal alkyls (M = Ti, Zr, or Hf) with bulky ligands, R, range from 44 kcal mol⁻¹ for Ti, R = neopentyl to 75 kcal mol⁻¹ for Zr, R = CH₂SiMe₃. Zr forms stronger bonds with C (by ca. 15%) than Ti.^{28a} It is interesting (i) that whereas bond strengths decrease upon descending a group of typical elements (e.g., Ge > Sn > Pb), the reverse trend is found in a transition-metal group (e.g., Ti < Zr < Hf), and (ii) that steric effects influence bond strengths (Me₃CCH₂ < Me₃SiCH₂). Microcalorimetric measurements have been

²⁸ (a) M. F. Lappert, D. S. Patil, and J. B. Pedley, *J.C.S. Chem. Comm.*, 1975, 830; (b) F. A. Adedigi, D. L. S. Brown, J. A. Connor, M. L. Leung, I. M. Paz-Andrade, and H. A. Skinner, *J. Organometallic Chem.*, 1975, **97**, 221; (c) J. Tamas, G. Czira, A. Mal'tsev, and O. M. Nefedov, *Magyar Kém. Folyóirat*, 1974, **80**, 439, (*Chem. Abs.*, 1975, **82**, 24 962j); (d) R. A. Burnham and S. R. Stobart, *J. Organometallic Chem.*, 1975, **86**, C45.

made on arenechromium tricarbonyl compounds, and bond enthalpy contributions derived.^{28b} These decrease as the donor power of the arene decreases from 55(4) kcal mol⁻¹ for the arene-metal bond of the hexamethylbenzene complex to 38(5) kcal mol⁻¹ for the corresponding bond of the chlorobenzene derivative. Mass spectrometric data were used to determine the dissociation energy of the Ge—C bond in Cl₃GeMe, which was found to be 66 kcal mol⁻¹.^{28c} Metal-metal bond dissociation energies have also been obtained by the mass spectrometer technique for the species Me₃M¹M²(CO)_n, as follows, $D(M^1-M^2)/\text{kcal mol}^{-1}$: Ge—Co, 73.8; Si—Co, 64.6; Si—Re, 71.5; Ge—Re, 73.8; and Sn—Re, 85.3.^{28d}

16 Olefin Metathesis

The remarkable catalytic disproportionation of olefins continues to attract considerable attention, and two reviews of the process have appeared.^{29a,b} The question of mechanism in this process is one of the most fascinating aspects, and several have been advanced, including cyclobutane-metal complexes and metallocyclic species in the transition state.^{29a} In 1972, a mechanism for the dismutation of electron-rich olefins was advanced which involved one-carbon transfers, and a metal-carbene was identified as an intermediate.^{29c} However, the unusual nature of the olefins and the low activation energy of the process for other olefins left it an open question as to whether the mechanism would have wider connotation. Two groups have reported findings which do lend support to this type of mechanism. The distribution of deuterium in the products of metathesis of [1,1,8,8-²H₄]octa-1,7-diene with octa-1,7-diene using the catalyst systems WCl₆-BuⁿLi-benzene and PhWCl₃-AlCl₃ is consistent (agreement is particularly good for the latter catalyst) with the single-C transfer idea.^{29d} Similar conclusions have also been reached from determination of product ratios with time in an experiment in which cyclo-octene, *trans*-but-2-ene, and *trans*-oct-4-ene disproportionated with a Mo-Al catalyst.^{29e} The authors also point out that the formation of catenanes in the disproportionation reaction can be simply accounted for by cyclization of a terminal carbene with an *internal* double bond. Further experimental data will be needed before it is possible to say whether the dismutation of alkynes is likely to occur through carbyne intermediates. The photochemical generation of an olefin dismutation catalyst requiring no co-catalyst has been reported.^{29f,g} Now photolysis of W(CO)₆ in CCl₄ has been found to give Cl₂W(CO)₄, which catalyses the reaction upon thermal or photochemical activation.^{29h} A brief description of the olefin metathesis reaction interpreted as a synchronous process has been given.^{29j}

17 Metal-Metal Bonds and Clusters

The chemistry of compounds containing intermetallic bonds is once again an area of great activity. (For metal carbonyl clusters see Section 20; see also Chapter 7,

²⁹ (a) R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.*, 1975, **4**, 155; (b) J. C. Mol and J. A. Moulijn, *Adv. Catalysis*, 1975, **24**, 131; (c) D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 927; (d) R. H. Grubbs, P. L. Burk, and D. D. Carr, *J. Amer. Chem. Soc.*, 1975, **97**, 3265; (e) T. J. Katz and J. McGinnis, *ibid.*, 1975, 1592; (f) A. A. Agapiou and E. McNelis, *J.C.S. Chem. Comm.*, 1975, 187; (g) P. Krausz, F. Garnier, and J. E. Dubois, *J. Amer. Chem. Soc.*, 1975, **97**, 437; (h) A. A. Agapiou and E. McNelis, *J. Organometallic Chem.*, 1976, **99**, C47; (j) F. D. Mango, *Coordination Chem. Rev.*, 1975, **15**, 142.

pp. 154 and 161.) The chemistry of systems having quadruple and other metal-metal bonds of high order has been reviewed.^{30a} A number of bimetallic and metal cluster compounds, particularly with metals of Main Groups II and III have bridging carbonyls of novel geometry. The crystallographic identification of a carbonyl group bridging two Mn atoms with both C and O interacting with one of the metal centres was noted for the first time (for details see below).^{30b} In certain situations the spectroscopic identification of bridging carbonyls may not be simple. Reaction of trimethylaluminium or dimethylaluminium hydride with $\text{CpW(CO)}_3\text{H}$ gives $[\text{CpW(CO)}_3\text{AlMe}_2]_2$. This compound contains rings of 12 atoms $(\text{WCOAlOC})_2$, each aluminium having two methyl substituents and the tungsten atoms an additional carbonyl and the cyclopentadienyl group. The rings are easily cleaved by protic species HX , affording the tungsten hydride and $(\text{Me}_2\text{AlX})_n$, while donors trimethylamine and diethyl ether yield the adducts of the AlW monomer unit.^{30c} The structure of the ring compound is unusual in that two of the carbonyl bridges are very close to linear ($173\text{--}176^\circ$). In the reaction of trimethylgallium with the same tungsten hydride, the compound $\text{CpW(CO)}_3\text{GaMe}_2$ is formed,^{30d} and this has been shown to have a Ga—W bond.^{30e} In hot hydrocarbon solution decomposition to yield $[\text{CpW(CO)}_3]_2\text{GaMe}$ and $[\text{CpW(CO)}_3]_3\text{Ga}$ occurs, neither of which, like $[\text{CpW(CO)}_3]_3\text{In}$,^{30f} shows i.r. bands due to bridging carbonyl ligands. The four-metal gallium system has three Ga—W bonds lying in a plane, the molecule (apart from the cyclopentadienyl rings) having roughly C_{3h} symmetry.^{30d} Magnesium resembles aluminium in forming several compounds linked to a transition metal *via* a Mg—O—C—M bridge, and, *e.g.*, the crystal structure of $(\text{py})^4\text{Mg}[\text{Mo(CO)}_3\text{Cp}]_2$ has established this type of bonding in a *trans*-arrangement about approximately octahedral magnesium.^{30g} The conditions favourable for the formation of M—C—O—Mg bonds have now been examined, and several useful synthetic approaches described.^{30h} The solubility of the magnesium compounds in hydrocarbon solvents makes them potentially very useful in metallation reactions where polar solvents are not suitable.

It has been remarked that lithium is capable of stabilizing unusual transition-metal compounds, notable among which are polynuclear species such as $\text{Li}_4\text{Cr}_2\text{Me}_8\cdot 4\text{THF}$,^{30j} $\text{Li}_6\text{Ni}_2\text{N}_2(\text{C}_6\text{H}_6)_2\cdot 2\text{Et}_2\text{O}$,^{30k} and $\text{Li}_4\text{Mo}_4\text{C}_{40}\text{H}_{44}$.^{30l} In such structures the interactions of the organic groups with the lithium atoms may be more significant than the base-lithium, and it is noteworthy that in a neutron and X-ray diffraction study of LiBMe_4 the bridging of lithium atoms by both linear $\text{Li—CH}_3\text{—B}$ and double and triple H-bridges is found.^{30m} The authors note the well-known reactivity of C—H when β to early main-group or transition metals, and point out that electron-deficient structures can become co-ordinatively saturated by the interaction of alkyl H atoms with metals. In this respect lithium shows strong Lewis

³⁰ (a) F. A. Cotton, *Chem. Soc. Rev.*, 1975, **4**, 27; (b) R. Colton, C. J. Commons, and A. F. Hoskins, *J.C.S. Chem. Comm.*, 1975, 363; (c) A. J. Conway, G. J. Gainsford, R. R. Schrieke, and J. D. Smith, *J.C.S. Dalton*, 1975, 2499; (d) A. J. Conway, P. B. Hitchcock, and J. D. Smith, *ibid.*, p. 1945; (e) Personal communication to the authors of ref. 30d by J. P. Oliver; (f) A. T. T. Hsieh and M. J. Mays, *J. Organometallic Chem.*, 1972, **37**, 9; (g) S. W. Ulmer, P. M. Sharstad, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1973, **95**, 4469; (h) G. B. McVicker, *Inorg. Chem.*, 1975, **14**, 2087; (j) F. Mein and K. Schmiedenkecht, *J. Organometallic Chem.*, 1966, **6**, 45, and refs. therein; (k) K. Jonas, *Angew. Chem. Internat. Edn.*, 1973, **12**, 997; (l) C. Prout and M. L. H. Green, *J.C.S. Chem. Comm.*, 1973, 259; (m) W. E. Rhine, G. Stucky, and S. W. Pederson, *J. Amer. Chem. Soc.*, 1975, **97**, 6401; (n) F. Armitage, 'Inorganic Rings and Cages', E. Arnold, London, 1972, and refs. therein.

acidity towards the weakly basic hydrogen atoms of hydrocarbon chains, and in the structure investigated each lithium atom has 10 hydrogen atoms within its first co-ordination sphere [6 at 2.234(10) Å and 4 at 2.115(8) Å].^{30m}

The tetrahedral P_4 can be substituted by various groups affording cluster compounds of which those structurally examined are edge-substituted species (see Chapter 6, p. 121).³⁰ⁿ

18 Shorter Topics

The structure of the dilithium derivative of the hexatriene dianion involves a planar geometry for four hydrogens and carbons of the anion and lithium interactions with four of the C atoms.³¹ Two structural studies of bis(cyclopentadienyl)magnesium have appeared; the gas-phase electron diffraction data indicate eclipsed cyclopentadienyl rings but do not completely exclude the staggered configuration,^{32a} while X-ray data, for the crystal at least, show a staggered ring arrangement.^{32b} Microwave examination of $CpBeH$ and isotopically labelled species shows a dipole moment of 2.08(1) D, and a $Be-H$ distance of 1.32(1) Å, the molecule having the expected C_{5v} geometry.^{32c} The existence of Grignard analogues for strontium and barium has been suggested in the literature, and THF adducts have now been reported, obtained from the finely divided metal and alkyl iodides at $-78^\circ C$. The compounds have low solubility and thermal stability, but are solvolysed with production of alkane using protic solvents, and afford low yields of tertiary alcohols on treatment with ketones.^{33a} The reaction of indene with calcium bis(tetraethyl)aluminum gives an indenylaluminum compound $(LAlEt_3)_2Ca(AlEt_4)$ (L = indenyl), which disproportionates easily, losing Et_3Al .^{33b} Perfluoroalkyl iodides react with calcium amalgam to give the perfluoroalkylcalcium iodides, as evidenced by their reactions with carbonyl compounds, which in some cases proceed in good yield, suggesting that the reagents may have potential value as perfluoroalkylating species.^{33c} When the Grignard reagents $RMgX$ (R = 3-phenyl-1-propyl or 1-phenyl-2-propyl) are irradiated in the $Mg-C$ chromophore region (*ca.* 254 nm) terminal olefins and $HMgX$ are formed, the latter disproportionating. The elimination reaction is 99% (or more) a β -elimination process, established by D-labelling studies.^{33d}

Several structural studies of tin(II) compounds appeared during 1975, mostly of compounds with co-ordination number for Sn of 4 or more. An interesting compound is $(C_6H_6)_2Sn(AlCl_4)_2C_6H_6$, in which the tin atom has approximate pentagonal-bipyramidal co-ordination, one axial position being the centre of a benzene ring, making appropriate the description ' π -benzene complex of tin(II)'.³⁴

N.m.r. studies of the dynamic equilibrium in $Cp_2M(BH_4)_2$ ($M = Zr$ or Hf) and $Cp_2Zr(H)BH_4$ have revealed a new type of borohydride exchange in which hydrogens of the cyclopentadienyl ring exchange with those of the BH_4 group. The

³¹ S. K. Akora, R. B. Bates, W. A. Beavers, and R. S. Cutler, *J. Amer. Chem. Soc.*, 1975, **97**, 6271.

³² (a) A. Haaland, J. Luszyk, J. Brunvon, and K. B. Starowieyski, *J. Organometallic Chem.*, 1975, **85**, 279; (b) W. Bünder and E. Weiss, *ibid.*, 1975, **92**, 1; (c) T. C. Bartke, A. Bjoerseth, A. Haaland, K. M. Marstokk, and H. Moelendal, *ibid.*, 1975, **85**, 271.

³³ (a) B. G. Gowenlock, W. E. Lindsell, and B. Singh, *J. Organometallic Chem.*, 1975, **101**, C37; (b) L. I. Zakharkin, Y. S. Zavizion, and L. L. Ivanov, *Zhur. obshchei Khim.*, 1975, **45**, 1900; (c) G. Santini, M. Le Blanc, and J. G. Riess, *J.C.S. Chem. Comm.*, 1975, 678; (d) B. O. Wagner and G. S. Hammond, *J. Organometallic Chem.*, 1975, **85**, 1.

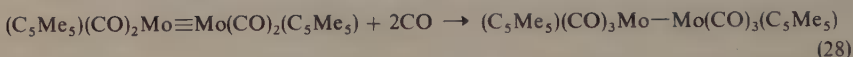
³⁴ P. F. Rodesiler, T. Auel, and E. L. Amma, *J. Amer. Chem. Soc.*, 1975, **97**, 7405.

predominantly unimolecular process is thought to occur *via* $\eta^1\text{-C}_5\text{H}_4\text{M}$ carbene (or ylide) intermediates. It also occurs, but more slowly, in the solid phase for $\text{Cp}_2\text{Zr}(\text{BD}_4)_2$.^{35a} Reactions between Cp_2ZrCl_2 and Et_3Al have been reported to yield a range of alkyl aluminium and zirconium species, including one with a 16-membered ring containing four Al and two Zr atoms. Structural evidence based on n.m.r. spectra is described.^{35b,c}

Monomeric paramagnetic carbonyls of vanadium are a unique group, and to date no dimeric carbonyl derivatives can be regarded as established. However, the chemistry of these species has been little studied, owing to the lack of a reactive and suitable starting material. Photosubstitution of the carbonyl anion $[\text{V}(\text{CO})_6]^-$ by *o*-phenylenebis(dimethylarsine), (diars), affords the thermally stable, anion $[\text{V}(\text{CO})_4(\text{diars})]^-$, which affords the first alkyl or η^3 -allyl carbonyl derivatives of V on treatment with methyl iodide or allyl chloride, respectively.^{36a} The ion Cp_2V^+ , which is isoelectronic with the monomeric form of titanocene, has been isolated from aqueous media in the form of adducts $[\text{VCp}_2\text{L}]^+$, ($\text{L} = \text{H}_2\text{O}$, acetone, or pyridine). The π -basicity of these species is shown by their ready conversion into the known cation $[\text{Cp}_2\text{V}(\text{CO})_2]^+$, and also into isocyanide or phosphine complexes.^{36b} The preparation of phenylvanadium dichloride by reaction of diphenyl-lithium with vanadium(IV) chloride has been reported, but the solid appears to be a co-ordination polymer.^{36c}

Niobium(V) chloride reacts with the cyclo-octatetraene anion to yield $\text{M}^+[\text{Nb}(\text{cot})_3]^-$, the first cyclo-octatetraene complex of the Group VA metals. A crystal study shows a trigonal arrangement of the ligands, with two η^3 -bonded and one η^4 -bonded, although the molecule is fluxional in solution. Reactions with phosphines and hydrogen afforded no characterizable vanadium compounds, although with CO salts of the $[\text{V}(\text{CO})_6]^-$ anion were isolated.^{37a} A new low-pressure synthesis of Cp_2NbH_3 from Cp_2NbCl_2 has been reported to give yields up to 55% after hydrolysis with aqueous NaOH. The insertion of acetylenes into the Nb—H bond and the reactions of the vinyls so formed are described.^{37b}

The reversible addition of carbon monoxide (2 mol) across a Mo—Mo bond is the first reported example of this type of process [equation (28)]. The forward reaction



can be induced by visible light or thermally,^{38a} while there is precedent for the reverse.^{38b} The reverse reaction, which is also photochemical, probably involves cleavage of the Mo—Mo bond, and photolysis of the hexacarbonyl species in carbon tetrachloride yields the species $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3\text{Cl}$.^{38a} Phosphines or phosphites also react with the tetracarbonyl complex (with C_5H_5) contrary to earlier

³⁵ (a) T. J. Marks and J. R. Kolb, *J. Amer. Chem. Soc.*, 1975, **97**, 2397; (b) W. Kaminsky and H. Sinn, *Annalen*, 1975, 429; (c) W. Kaminsky and H. J. Vollmer, *ibid.*, p. 438.

³⁶ (a) J. E. Ellis and R. A. Faltynek, *J. Organometallic Chem.*, 1975, **93**, 205; (b) G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1975, 578; (c) S. Schroeder, A. Lachowitz, and K. H. Thiele, *Z. anorg. Chem.*, 1975, **415**, 104.

³⁷ (a) L. J. Guggenberger and R. R. Schrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6693; (b) J. A. Labinger and J. Schwartz, *ibid.*, p. 1596.

³⁸ (a) D. S. Ginley and M. S. Wrighton, *J. Amer. Chem. Soc.*, 1975, **97**, 3533; (b) P. Hackett, P. S. O'Neill, and A. R. Manning, *J.C.S. Dalton*, 1974, 1625; (c) R. J. Klinger, W. Butler, and M. D. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 3535; (d) T. Ito and A. Yamamoto, *J.C.S. Dalton*, 1975, 1398; (e) D. L. Lewis and S. J. Lippard, *J. Amer. Chem. Soc.*, 1975, **97**, 2697.

reports.^{38c} Acetylenes react forming bridged dimolybdenum derivatives. The X-ray structure determination of the tetracarbonyl compound with unsubstituted cyclopentadienes confirms the triple-bonded formulation, $\text{Mo}\equiv\text{Mo} = 2.448(1) \text{ \AA}$.^{38c} (For further photochemistry of metal carbonyls see Section 20.)

The reactions of $\text{Mo}(\text{C}_2\text{H}_4)(\text{dppe})_2$ with a number of reagents have been examined, among which the contrasting thermal {to give *cis*- $[\text{Mo}(\text{CO}_2(\text{dppe})_2)]$ } and photochemical (to give an uncharacterized CO_2 adduct) behaviour with carbon dioxide is noteworthy.^{38d} The structure of $[(\text{Bu}^t\text{NC})_7\text{Mo}]^+\text{PF}_6^-$ shows the same co-ordination polyhedron as had been established for the iodohexakis(iso-cyanide)molybdenum(II) cation, *i.e.*, a monocapped trigonal prism.^{38e}

There is much evidence to suggest that tungstenocene is an intermediate in the reactions (both thermal and photochemical) of a number of species Cp_2WX_n (X_n includes H_2 , CO , and Cl_2), and is highly reactive, for example inserting into the C—H bonds of mesitylene or *p*-xylene.^{39a} The photo-induced insertion of tungsten into methanol has been shown to give both $\text{Cp}_2\text{W}(\text{H})\text{OMe}$ and $\text{Cp}_2\text{WMe}(\text{OMe})$, probably *via* the insertion of tungstenocene into the O—H and C—H bonds of methanol respectively.^{39a} Alkyl- and acyl-pentacarbonyltungsten anions have been obtained by two routes: treatment of the corresponding halide anions with organolithium reagent, and photolysis of the appropriate neutral species $(\text{OC})_5\text{WCOR}$.^{39b} Reactions with HCl , trityl tetrafluoroborate, CO , or PPh_3 are reported for some of the anions.

The reaction of dibenzylmagnesium with tungsten tetrachloride affords tetrabenzyltungsten.^{39c} Other reports on homoleptic metal alkyls and organometallic compounds in high oxidation states (including tungsten) are covered in Section 22.

19 Books and Reviews: Main-Group and Early Transition Elements

Among many review articles on the subject matter of this Chapter, the following are among the most directly relevant. Matteson's book on organometallic reaction mechanisms of the non-transition elements presents a critical review of its subject including the elements B and Si, but not P.⁴⁰ Other books include works on organometallic reactions,⁴¹ and organometallic compounds of the transition elements and related aspects of catalysis.⁴² A new edition of 'Bažant' has appeared, reviewing the Si literature since 1961.⁴³

The organometallic chemistry of the main-group elements has been reviewed,⁴⁴ and articles dealing with aspects of this area cover synthesis and reactions of organo-lithium reagents derived from weakly acidic C—H compounds,⁴⁵ and

³⁹ (a) L. Farrugia and M. L. H. Green, *J.C.S. Chem. Comm.*, 1975, 416, and refs. therein; (b) C. P. Casey, S. W. Polichnowski, and R. L. Anderson, *J. Amer. Chem. Soc.*, 1975, **97**, 7375; (c) K. H. Thiele, A. Russek, R. Opitz, B. Mohai, and W. Brueser, *Z. anorg. Chem.*, 1975, **412**, 11.

⁴⁰ D. S. Matteson, 'Organometallic Reaction Mechanisms of Non-transition Elements', Academic Press, New York, 1974.

⁴¹ 'Organometallic Reactions', ed. E. I. Becker and M. Tsutsui, Wiley, New York, 1975.

⁴² B. L. Shaw and N. L. Tucker, 'Organo-transition Metal Compounds and Related Aspects of Catalysis', Pergamon, New York, 1975.

⁴³ V. Bažant, J. Hetflejš, V. Chvalovsky, J. Joklik, O. Kruchna, J. Rathousky, and J. Schraml, 'Handbook of Organo-silicon Compounds. Advances since 1961', Vol. 1, Dekker, New York, 1975.

⁴⁴ J. D. Smith and D. R. M. Walton, *Adv. Organometallic Chem.*, 1975, **13**, 453.

⁴⁵ D. Ivanov, G. Vasilev, and I. Panaiotiev, *Synthesis*, 1975, 83.

cyclopolyarsines.⁴⁶ In the series edited by Nesmayanov and Kocheskov the organic chemistry of Tc,⁴⁷ Ta,⁴⁸ lanthanides,^{17c} Nb,⁴⁹ Hf,⁵⁰ V,⁵¹ and Zr⁵² has been described. The *Journal of Organometallic Chemistry* annual review series continues. Organometallic compounds with bonds between transition metals and elements of Group IIIB have also been surveyed.⁵³

20 Metal Carbonyls

Matrix Isolation of Radical Species, other Metal Carbonyl Transients.—Interest in paramagnetic carbonyl complexes and in unstable carbonyls in general has accelerated in recent years with the development of methods for treating metal atoms with various substrates (see also Section 2), and also with the development of carbonyl photochemistry. $\text{Mn}(\text{CO})_5$ in particular has been of interest to many research groups.⁵⁴ Originally suggested as a precursor of $[\text{Mn}(\text{CO})_5]^+$ in the mass spectrum of pyrolysed $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CO})_5$ had been proposed as an intermediate in a number of chemical reactions of $\text{Mn}_2(\text{CO})_{10}$, and an e.s.r. spectrum obtained from 350 nm photolysis of $\text{Mn}_2(\text{CO})_{10}$ in THF had been assigned to the pentacarbonyl. A report this year^{55a} disputes this e.s.r. assignment and suggests that the six-line spectrum is actually due to an Mn^{II} species, $[\text{Mn}(\text{THF})_6]^{2+}$. The spectrum is remarkable because of its very narrow hyperfine lines. An alternative^{55b} approach to the problem *via* homolysis of the $\text{M}-\text{C}$ bond of $[\text{RMn}(\text{CO})_5]$ ($\text{R} = \text{Me}$ or PhCH_2) has yielded e.s.r. evidence for the generation of $\text{Mn}(\text{CO})_5$. U.v. irradiation in the presence of the spin trap, nitrosodurene, gives e.s.r. spectra of the nitroxides, $\text{ArN}(\text{O})\text{Mn}(\text{CO})_5$ and $\text{ArN}(\text{O})\text{R}$ ($\text{Ar} = 2,3,5,6\text{-Me}_4\text{C}_6\text{H}$), but the spectrum of the free $\text{Mn}(\text{CO})_5$ radical has still not been observed.^{55b} [Similarly, photolysis of vitamin B_{12} coenzyme, 5'-deoxyadenosylcobalamin, or ethylcobalamin, in aqueous medium in presence of $\text{Bu}'\text{NO}$ as spin trap, has afforded the 5'-deoxyadenosyl($\text{Bu}'\text{NO}$ or $\text{Et}(\text{Bu}')\text{NO}$, respectively.^{55c}]

The characterization of $\text{Mn}(\text{CO})_5$ has now been achieved by matrix-isolation techniques.⁵⁴ Using an $\text{Mn}:\text{CO}$ ratio of $1:10^4$ or less, condensed in an argon matrix, the principal species is $\text{Mn}(\text{CO})_5$, and at higher $\text{Mn}:\text{Co}$ ratios the dinuclear $\text{Mn}_2(\text{CO})_{10}$ or 2 species are obtained. I.r. spectra of the pentacarbonyl indicate a square-pyramidal structure, and this observation completes the characterization of the series of pentacarbonyls of the first transition series from vanadium to iron (see Table 1, p. 220).⁵⁴ An alternative trigonal-bipyramidal form of $\text{Cr}(\text{CO})_5$ has been claimed to exist but it now seems likely that this is incorrect.⁵⁶ Thus there is a clear

⁴⁶ L. R. Smith and J. L. Mills, *J. Organometallic Chem.*, 1975, **84**, 1.

⁴⁷ A. A. Ioganson, K. N. Anisimov, and N. E. Kolobova, *Metody. Elem.-Org. Khim.*, 1974, **2**, 851.

⁴⁸ A. A. Pasinskii, *Metody Elem.-Org. Khim.*, 1974, **1**, 453.

⁴⁹ A. A. Pasinskii, *Metody Elem.-Org. Khim.*, 1974, **1**, 434.

⁵⁰ E. M. Brainina, *Metody Elem.-Org. Khim.*, 1974, **1**, 373.

⁵¹ A. A. Pasinskii, *Metody Elem.-Org. Khim.*, 1974, **1**, 389.

⁵² E. M. Brainina, *Metody Elem.-Org. Khim.*, 1974, **1**, 320.

⁵³ A. T. T. Hsieh, *Inorg. Chim. Acta*, 1975, **14**, 87.

⁵⁴ H. Huber, E. P. Kündig, G. A. Ozin, and A. J. Poë, *J. Amer. Chem. Soc.*, 1975, **97**, 308, and references therein.

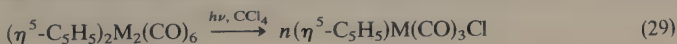
⁵⁵ (a) A. Hudson, M. F. Lappert, and B. K. Nicholson, *J. Organometallic Chem.*, 1975, **92**, C11; (b) A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J.C.S. Chem. Comm.*, 1974, 966; (c) K. N. Joblin, A. W. Johnson, M. F. Lappert, and B. K. Nicholson, *ibid.*, p. 441.

⁵⁶ J. D. Black and P. S. Braterman, *J. Amer. Chem. Soc.*, 1975, **97**, 2908.

correlation of stereochemistry with electron configuration, and this is expected in terms of the generally accepted MO sequences for trigonal-bipyramidal and square-pyramidal complexes. Assuming low-spin configurations, the 15- and 17-electron trigonal-bipyramidal forms should be subject to first-order Jahn–Teller distortion towards a square-pyramidal form and the 16-electron complexes are stable to second-order Jahn–Teller distortions only in the square-pyramidal configuration. The 18-electron species should exhibit second-order instability in both D_{3h} and C_{4v} forms, and this is considered to account for the well-known facile interchange of axial and equatorial CO groups.⁵⁴ Similar conclusions regarding the relationship between electron configuration and geometry in $M(CO)_5$ species have been reached as part of a wide-ranging theoretical study of $M(CO)_3$, $M(CO)_4$, and $M(CO)_5$ carbonyl fragments using extended Hückel calculations.⁵⁷ Among the many topics covered by this study is a rationalization of the preferences of $Fe(CO)_3$ and $Cr(CO)_4$ fragments for bonding with conjugated and non-conjugated dienes, respectively.

In other matrix-isolation studies, the range of binary carbonyls has been extended along the transition series to copper, the species characterized being $Cu(CO)_{1-3}$ and $Cu_2(CO)_6$. The latter is the dinuclear carbonyl which would be predicted to follow $Ni(CO)_4$.⁵⁸

Photochemistry.—Metal-centred radicals of the $Mn(CO)_5$ and related types may also be generated in photochemical processes. Of the large amount of reported work on photochemistry of metal carbonyls,⁵⁹ relatively little is concerned with homolysis of metal–metal bonds to yield metal-centred radicals. For example, previous studies on photolytic reactions of $M_2(CO)_{10}$ species ($M = Mn$ or Re) have yielded both simple substitution products, such as $Mn_2(CO)_9(PPh_3)$ from $Mn_2(CO)_{10}$ and PPh_3 , and mononuclear products resulting from cleavage of the $M-M$ bond, such as $ReCl(CO)_5$ from $Re_2(CO)_{10}$ and CCl_4 . These reports were qualitative in nature, and quantitative studies giving definitive evidence for the primary photochemical processes were not available. A series of studies reported this year⁶⁰ presents evidence that the primary process in photochemical reactions of $M_2(CO)_{10}$ ($M = Mn$ or Re), $Mn_2(CO)_9(PPh_3)$, $Mn_2(CO)_8(PPh_3)_2$, $MnRe(CO)_{10}$, $[(\eta^5-C_5H_5)M(CO)_3]_2$, ($M = Mo$ or W), and $(OC)_5M^1M^2(CO)_3(\eta^5-C_5H_5)$ ($M^1 = Mn$ or Re and $M^2 = Mo$ or W), is homolytic cleavage of the metal–metal bond. Results for the $[(\eta^5-C_5H_5)M(CO)_3]_2$ complexes are typical. These molecules have an intense, fairly narrow, near-u.v. absorption (*ca.* 20 000 cm^{-1}) which has no analogue in $(\eta^5-C_5H_5)M(CO)_3Cl$ complexes and is assigned to a one-electron transition which is essentially $\sigma \rightarrow \sigma^*$ with respect to the $M-M$ bond. Photolysis results in excitation of this transition with consequent bond homolysis. The principal evidence is: (i) photolysis in CCl_4 solution proceeds according to equation (29), where n is very near 2.0 and the chloride is the



sole photoproduct; (ii) photolysis in the presence of Ph_3CCl gives e.s.r. evidence for formation of $Ph_3C\cdot$ and in the presence of $PhCH_2Cl$ the products are $PhCH_2CH_2Ph$ and $(\eta^5-C_5H_5)M(CO)_3Cl$; and (iii) photolysis of mixtures of $[(\eta^5-C_5H_5)M^1(CO)_3]_2$

⁵⁷ M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

⁵⁸ H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, 1975, **97**, 2097.

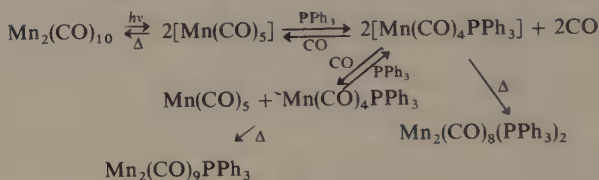
⁵⁹ M. Wrighton, *Chem. Rev.*, 1974, **74**, 401, and references therein.

⁶⁰ M. S. Wrighton and D. S. Ginley, *J. Amer. Chem. Soc.*, 1975, **97**, 2065, 4246, 4908.

with $M_2^2(CO)_{10}$ ($M^1 = Mo$ or W , $M^2 = Mn$ or Re) gives all four M^1-M^2 species, $(\eta^5-C_5H_5)M^1(CO)_3-M^2(CO)_5$, in high yields based on the disappearance of homonuclear species.

The 17-electron intermediates generated in these photolytic reactions may be compared with the well-known and important catalytic species $[Co(CN)_5]^{3-}$. Reactions of the latter with alkyl halides (RX) are known to proceed by radical pathways giving both $[Co(CN)_5R]^{3-}$ and $[Co(CN)_5X]^{3-}$. The difference between this process and the reactions of $M(CO)_5$ ($M = Mn$ or Re) or $(\eta^5-C_5H_5)M(CO)_3$ ($M = Mo$ or W) with $PhCH_2Cl$ to yield $PhCH_2CH_2Ph$ and $M(CO)_5Cl$ or $(\eta^5-C_5H_5)M(CO)_3Cl$ is attributed to the very low steady-state concentration of metal radicals in the latter experiments. This renders coupling of metal and organic radicals an unlikely process.⁶⁰ The comparison with $[Co(CN)_5]^{3-}$ is strengthened by the discovery that $Re(CO)_5$, generated by irradiation of $Re_2(CO)_{10}$ at 311 nm, is capable of activating molecular hydrogen. The proposed mechanism involves dissociation of CO from $Re(CO)_5$, oxidative addition of H_2 to the resulting $Re(CO)_4$, species and subsequent reaction to $ReH(CO)_5$, $H_2Re_2(CO)_8$, and $H_3Re_3(CO)_{12}$.⁶¹

The apparent conflict between the above processes requiring $M-M$ bond homolysis as the primary photochemical process and previous reports of heterolysis and substitution reactions is considered to be due to the possibility of secondary thermal reactions. For example, Scheme 6 is proposed⁶⁰ to account for photosubstitution in $Mn_2(CO)_{10}$. An independent flash photolysis study⁶² of $[(\eta^5-C_5H_5)Mo(CO)_3]_2$ is slightly at variance with these suggestions in that two intermediates were detected, both of which react by independent thermal processes to



Scheme 6

regenerate the starting complex. One of these is assigned as $(\eta^5-C_5H_5)Mo(CO)_3$ and the other as $(\eta^5-C_5H_5)_2Mo_2(CO)_5$, but it is not certain that the latter is a primary photoproduct.⁶² However, the possibility of substitution *via* homolysis has been further supported by studies of the reactions of $[Mn(CO)_4(PPh_3)]_2$ with $P(OPh)_3$ and of $ReH(CO)_5$ with PPh_3 .⁶³ Both reactions proceed by initial generation of radicals $M(CO)_4L$ ($M = Re$, $L = CO$; $M = Mn$, $L = PPh_3$), followed by associative ligand exchange at the reactive intermediate. This type of process was previously unknown for simple substitution reactions, which had been considered to proceed by straightforward dissociative or associative pathways involving the substrate species and no radical intermediates.⁶³

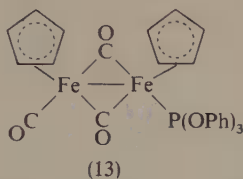
Fluxional Processes.—The possibility of 'carbonyl scrambling' as an important class of fluxional process was first pointed out in 1972 by Bullitt, Cotton, and Marks as a

⁶¹ J. L. Hughey, C. R. Bock, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1975, **97**, 4440.

⁶² B. H. Byers and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 3260.

⁶³ J. P. Fawcett, R. A. Jackson, and A. J. Poë, *J.C.S. Chem. Comm.*, 1975, 733; B. H. Byers and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 947.

result of studies on the carbonyl-bridged complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$. Since that time the ready availability of ^{13}C n.m.r. has led to a rapid expansion of knowledge in this area, the majority of studies being devoted to bridge-terminal interchanges involving migration of CO groups from one metal atom to another, particularly in dinuclear species. Typical of these studies are the observations for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ (13) and the similar results obtained by an independent group on the analogous triethyl phosphite complex.⁶⁴ In the solid state, the triphenyl phosphite complex has structure (13), but in solution i.r. and ^1H and ^{13}C



n.m.r. spectra show rapid interconversion between isomers having *cis* and *trans* arrangements of the cyclopentadienyl groups and simultaneous exchange of carbonyls between bridging and terminal sites. The generally accepted mechanism for processes of this type involves two essential steps: (i) concerted opening and closing of *pairs* of ligand bridges and (ii) hindered internal rotations in the non-bridged tautomers. If the above mechanism is correct, then *cis-trans* isomer interconversion and bridge-terminal CO exchange in (13) should occur at the same rate. This is observed experimentally and the above mechanism is thus well established, although no rationalization for the necessity of *concerted*, pairwise bridge opening and closing has been presented.⁶⁴ A survey of the stereochemistry of the compounds $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Y}]$, where Y can be a univalent group or may be a group capable of bridging to the iron, has now shown that the geometry in these species is consistently close to octahedral. This observation implies a rigidity in the local stereochemistry at iron and one consequence of this is that the tautomer interconversion mechanism for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ and related species must involve simultaneous making or breaking of two carbonyl bridge systems.⁶⁵ The mechanism of CO transfer in systems such as $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$, which involve only a single carbonyl bridge, is less well established. Intermediates involving a triple CO bridge have been proposed, but the facile CO site exchange in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2\{\text{P}(\text{OPh})_3\}]$, where such an intermediate requires a phosphite bridge, renders this process unlikely. Moreover, the ^{31}P n.m.r. spectrum of the phosphite complex is temperature invariant, indicating that the phosphite remains co-ordinated to one rhodium atom. The authors favour a mechanism involving formation of a new CO bridge, synchronous with the breaking of the existing bridge.⁶⁶

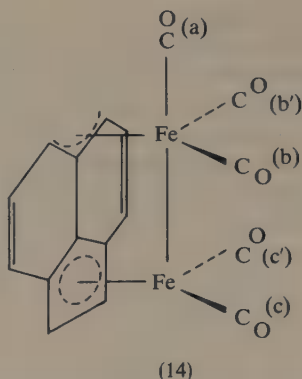
A fundamentally different type of carbonyl scrambling process has been demonstrated by a ^{13}C n.m.r. study of (14).⁶⁷ Several previous experiments had indicated that, in species having non-equivalent CO groups within $\text{M}(\text{CO})_3$ sets, site exchange

⁶⁴ F. A. Cotton, L. Kruczynski, and A. J. White, *Inorg. Chem.*, 1974, **13**, 1402, and references therein; D. C. Harris, E. Rosenberg, and J. D. Roberts, *J.C.S. Dalton*, 1974, 2398.

⁶⁵ J. R. Miller and F. S. Stephens, *J.C.S. Dalton*, 1975, 833.

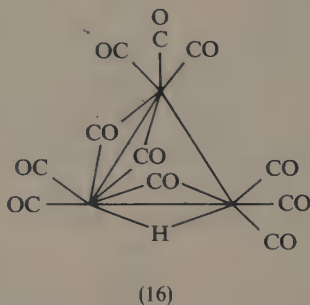
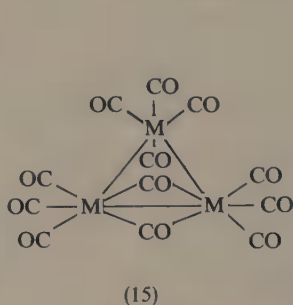
⁶⁶ J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1975, 576.

⁶⁷ F. A. Cotton, D. L. Hunter, and P. Lahuerta, *Inorg. Chem.*, 1975, **14**, 511, and references therein.



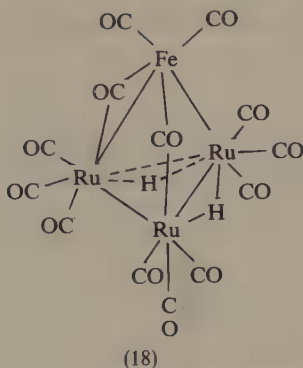
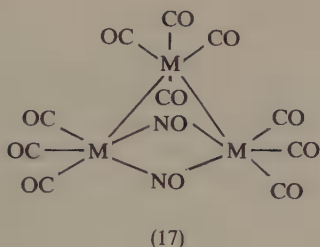
by a process equivalent to rotation of the $M(CO)_3$ fragment was a possibility. For the acenaphthylene complex (14) this process may be unambiguously demonstrated even though no other fluxional process (*e.g.* 'ring whizzing') is occurring. Between -60 and $+45^\circ\text{C}$, ^{13}C n.m.r. spectra show that three CO groups, a, b, and b', are interchanging but there is no interchange with the groups c and c'. The process is essentially rotation of the $\text{Fe}(CO)_3$ unit, and the more normal bridge-terminal mechanism is prevented by the unusually long Fe—Fe bond (2.77 \AA). The complex $\text{Fe}_2(CO)_6(\text{cycloheptatriene})$ also has an exceptionally long Fe—Fe bond (2.87 \AA) and is believed to represent another example of the same type of process, although in this case definite proof is lacking.⁶⁷

As noted above, the majority of the CO scrambling processes studied in detail have involved dinuclear complexes. Observations on trinuclear complexes were limited to the prediction and confirmation that the barrier to total CO scrambling in $\text{Fe}_3(CO)_{12}$ is $<5 \text{ kcal mol}^{-1}$, *i.e.* the system is still fluxional at -150°C .⁶⁸ Variable-temperature ^{13}C n.m.r. of $M_3(CO)_{12}$ ($M = \text{Fe, Ru, or Os}$) and related complexes has now shown that several different scrambling processes can operate.⁶⁹ $\text{Fe}_3(CO)_{12}$ has the solid-state structure (15) and it is therefore probable that scrambling occurs *via* pair-wise bridge-terminal interchange of the type discussed above. This type of mechanism is also required for $[\text{HFe}_3(CO)_{11}]^-$ (16) since the unique bridging CO is not involved in the interchange. However, an alternative



⁶⁸ F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, 1974, **11**, L9.

mechanism which is essentially a rotation of an $M(CO)_4$ group similar to that discussed above for $M(CO)_3$ groups is required by evidence on $[Ru_3(CO)_{10}(NO)_2]$ (17). This species exhibits three ^{13}C n.m.r. signals with relative intensity 4:4:2, indicating that localized exchange of axial and equatorial CO is occurring at the $Ru(CO)_4$ group. Since the $Ru(CO)_3$ groups are rigid, CO-bridged intermediates are clearly not involved.⁶⁹



Similar fluxional processes have been observed for tetranuclear species. For example, in $H_2FeRu_3(CO)_{13}$ (18) at least three carbonyl exchange processes can be distinguished, the most rapid (*ca.* $-70^\circ C$) localized at Fe, the next (*ca.* $-45^\circ C$) localized at the three Ru atoms, and the last general over all metal centres at $+95^\circ C$.⁷⁰ ^{13}C N.m.r. studies have also prompted a re-opening of the long-standing argument as to the solution structure of $Co_4(CO)_{12}$. At $-100^\circ C$ three equal-intensity resonances corresponding to one bridging and two terminal environments are observed, suggesting a structure with D_{2d} symmetry rather than the accepted structure with C_{3v} symmetry.^{71a} In contrast the ^{13}C n.m.r. spectrum of $Co_4(CO)_{11}[P(OMe)_3]$ at $-82^\circ C$ shows bridging:terminal CO groups in a ratio of 3:8, as expected for a C_{3v} structure with one of the basal terminal CO groups replaced by phosphite. The differences are most probably due to the difficulties of interpreting the relative intensities of n.m.r. lines affected by rapid ^{59}Co quadrupolar relaxation.^{71b}

Work on CO scrambling in larger clusters has also been reported this year.⁷² $Rh_6(CO)_{16}$ is not fluxional at $+70^\circ C$, whereas $[Rh_6(CO)_{15}]^{2-}$ undergoes rapid, complete carbonyl scrambling even at $-70^\circ C$. The structure of the anion is derived from the neutral species by removal of one face-bridging carbonyl, and this change is considered to make available intermediates involving minimal changes in symmetry and bonding. Another anion, $[Rh_7(CO)_{16}]^{3-}$, is intermediate between the other two species, being rigid at $-70^\circ C$, but undergoing partial CO exchange at $+25^\circ C$.⁷²

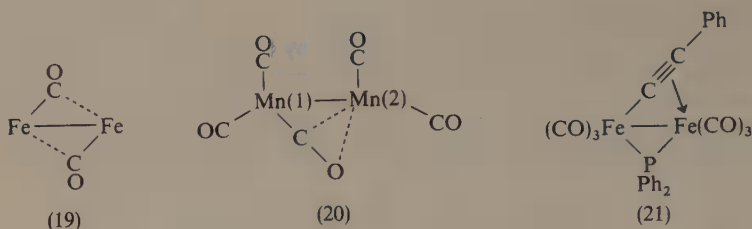
Bridging Carbonyl Structures.—The fundamental terminal and symmetrically bridging modes of carbonyl bonding have been known for a very long time, and more

⁶⁹ A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1042.

⁷⁰ L. Milone, S. Aime, E. W. Randall, and E. Rosenberg, *J.C.S. Chem. Comm.*, 1975, 452.

⁷¹ (a) J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Amer. Chem. Soc.*, 1975, **97**, 1245; (b) M. A. Cohen, D. R. Kidd, and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 4408.

⁷² B. T. Heaton, A. D. C. Towl, P. Chini, A. Fumagelli, D. J. A. McCaffrey, and S. Martinengo, *J.C.S. Chem. Comm.*, 1975, 523.



recently two additional types of co-ordination have been shown to be relatively common. Co-ordinated carbonyls may form bridges to main-group or other transition elements *via* oxygen bonding. Moreover, as reported last year, there exists a complete range of carbon-bridged types, varying from the normal symmetrical bridge to the very unsymmetrical bridges exemplified by (19). There are also examples where only one of a pair of bridging carbonyls is asymmetric and others where a single asymmetrical carbonyl is the only bridging group.⁷³ The product of reaction of $\text{Mn}_2(\text{CO})_{10}$ with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dpm) has the molecular formula $\text{Mn}_2(\text{CO})_5(\text{dpm})_2$, and appears to represent an important new type of carbonyl bridging structure.⁷⁴ The manganese atoms are bridged by the dpm groups so that the two manganese and four phosphorus atoms are almost coplanar. Approximately perpendicular to this plane is a plane containing the carbonyl groups [see (20)]. The Mn—Mn bond is 2.934 Å, comparable with that in $\text{Mn}_2(\text{CO})_{10}$, and the bridging carbonyl is apparently bound by a rather long σ -bond to Mn(1) [Mn(1)—C is 1.93 Å compared with an average 1.69 Å for the terminal Mn—C bonds] and *via* its π -electrons to Mn(2) [Mn(2)—C is 2.01 Å and Mn(2)—O is 2.20 Å].⁷⁴ Bonding to Mn(2) is thus similar to olefin or acetylene bonding and may be compared to structures such as (21).⁷⁵

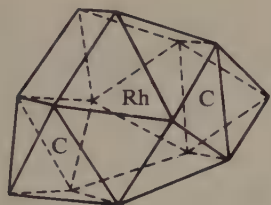
Cluster Carbonyl Structures.—One of the interesting features of cluster chemistry is the intermediate position which these complexes occupy between molecular species and metal lattices. In the long term this relation could lead to important results in the field of catalysis. However, most of the clusters studied to date have an essential difference from metallic lattices in that the metal atoms are arranged in one or other of the common co-ordination polyhedra and the centre of the polyhedron is unoccupied, *i.e.* there is no metal atom co-ordinated solely by other metals. Exceptions to this statement, such as the $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ ion, are fairly normal co-ordination complexes, and the environment of the central metal ion bears little relation to that of a metal in a metallic lattice. However, in recent years X-ray diffraction studies on gold clusters have been reported in which a polyhedron of gold atoms has another gold atom at its centre.⁷⁶ The geometries of both $[\text{Au}_6\{\text{P}(p\text{-MeC}_6\text{H}_4)_3\}_8][\text{PF}_6]_3$ and $[\text{Au}_{11}\text{I}_3\{\text{P}(p\text{-FC}_6\text{H}_4)_3\}]$ are derived from a centred icosahedron, in the former case by removal of four atoms constituting an equatorial rectangle

⁷³ F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 1233, 5070, and references therein.

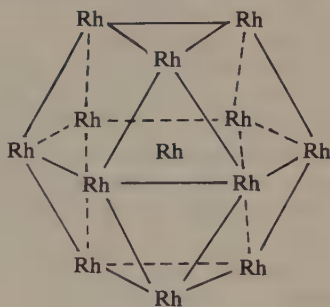
⁷⁴ R. Colton, C. J. Commons, and B. J. Hoskins, *J.C.S. Chem. Comm.*, 1975, 363; C. J. Commons and B. J. Hoskins, *Austral. J. Chem.*, 1975, **28**, 1663; R. Colton and C. J. Commons, *Austral. J. Chem.*, 1975, **28**, 1673.

⁷⁵ H. A. Patel, R. G. Fischer, A. J. Carty, D. V. Naik, and G. J. Palenik, *J. Organometallic Chem.*, 1973, **60**, C49.

and in the latter by replacement of one triangular face by a single gold atom.⁷⁶ $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ is the first metal cluster with a trigonal-prismatic arrangement of metal atoms, and its oxidation with Fe^{3+} has yielded several interesting products.⁷⁷ $[\text{Rh}_8(\text{CO})_{19}\text{C}]$ is related to the trigonal prism by capping one rectangular face and bridging one base edge. $[\text{Rh}_{15}(\text{CO})_{28}\text{C}_2]^-$ has the more complex geometry (22), in which the metal atoms form a centred, tetracapped pentagonal prism, and is the first example apart from the gold clusters above of a completely encapsulated metal atom. The mean distance from the central Rh to its 12 near neighbors is 2.90 Å. The analogy between this complex and a metal lattice is spoiled by the two carbide carbons which lie at 2.06 Å from the centre Rh.⁷⁷ However, in the structure (23) of the $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_3]^{2-}$ ion, derived from reaction of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ with hydrogen and studied by X-ray diffraction⁷⁸ of its $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt, the arrangement of rhodium atoms is essentially that found in hexagonal close-packing. The 13 rhodium atoms are located in three nearly parallel layers, making a cluster of D_{3h} idealized symmetry, and the central metal atom is surrounded by 12 metal atoms at mean distances of 2.81 Å. Comparison with the cubic close-packed distance of 2.69 Å in Rh metal indicates that the electron density is higher in the cluster.⁷⁸



(22)



(23)

The first example of a homonuclear, trigonal-bipyramidal metal cluster has been reported.⁷⁹ Reduction of $\text{Ni}(\text{CO})_4$ by alkali metals in THF gives $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and $[\text{Ni}_5(\text{CO})_{12}]^{2-}$ and X-ray diffraction study of the latter as its $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt reveals a trigonal-bipyramidal cluster of Ni atoms with three bridging and three terminal carbonyls symmetrically disposed in the equatorial plane and three terminal carbonyls on each axial Ni.⁷⁹

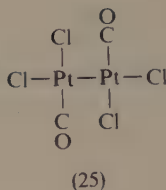
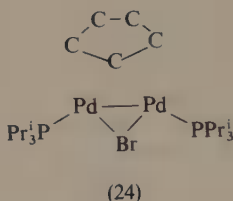
Platinum(II) and Palladium(II).—These are rare oxidation states, the former being previously represented only by $[\text{PtCl}(\text{PPh}_3)_2]_2$, $[\text{Pt}_2\text{Cl}_4(\text{CO})_2]^{2-}$, $[\text{Pt}_2\text{Cl}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$, and $[(\text{Ph}_3\text{P})_2\text{Pt}\cdot\text{S}\cdot\text{Pt}(\text{CO})(\text{PPh}_3)]$ and the latter by $[\text{Pd}_2\text{Cl}_2(\text{Bu}^+\text{NC})_4]$, $[\text{Pd}_2\text{Cl}_4(\text{CO})_2]^{2-}$, an ill defined species $[\text{Pd}(\text{C}_6\text{H}_6)(\text{H}_2\text{O})(\text{ClO}_4)]_n$, and some very unusual organo-bridged compounds, $[\text{Pd}_2(\text{C}_3\text{H}_5)(\text{PPh}_3)_2\text{I}]$ (A) and

⁷⁶ P. L. Bellon, M. Manassero, and M. Sansoni, *J.C.S. Dalton*, 1972, 1481; P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *J.C.S. Chem. Comm.*, 1971, 1423.

⁷⁷ V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J.C.S. Dalton*, 1975, 305, and references therein.

⁷⁸ V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo, and W. J. Anker, *J.C.S. Chem. Comm.*, 1975, 859.

⁷⁹ G. Longini, P. Chini, L. D. Lower, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 5034.



[PdAl₂Cl₇(C₆H₆)₂]₂ (B). X-Ray structure studies were available only on the sulphur-bridged platinum compound and the organo-bridged palladium compounds, the latter having structures analogous to (24), except for the replacement of the C₅H₅ and Br bridges by allyl and iodide in (A) and by two benzene bridges in (B). Moreover, all of the known compounds appear to be ligand bridged, with the observed diamagnetism indicating some metal-metal bonding.^{80,81} An X-ray structure determination carried out this year has confirmed the original suggestions (made in 1973 by Goggin and Goodfellow and based mainly on vibrational spectra) that the [Pt₂Cl₄(CO)₂]²⁻ ion contains an unsupported Pt—Pt bond and can exhibit an unusual form of isomerism. The anion was studied as its [NPr₄]⁺ salt and is of the basic structural type shown in (25). Co-ordination about each platinum is distorted square-planar, and the two planes are twisted about the Pt—Pt bond to give a *transoid* configuration with the dihedral angle between the two Pt—Cl groups being 120°. The complex studied was one of the two isomers originally isolated; the other is thought to have the related *cisoid* structure. The 120° angle is considered to be a compromise between repulsions due to filled interaxial *d*-orbitals (optimum angle, 135°) and interligand repulsions (optimum angle, 90°).⁸⁰ The closely related palladium(I) ion [Pd₂(CNCH₃)₆]²⁺ has a similar structure and is thus the first Pd^I dimer without bridging ligands in the solid state. Unlike the platinum complex, the two square planes are almost perpendicular (dihedral angle 86.2°), a situation akin to the Ni^I complex [Ni₂(CN)₆]²⁻ (dihedral angle 82°).⁸¹ The metal-metal bonds in both palladium and platinum complexes are among the shortest known (2.531 Å and 2.584 Å, respectively).

X-Ray structure determinations of [Pd₂(μ-Br)(μ-C₅H₅)(PPr₃ⁱ)₂] (24)⁸² and [Pd₂(μ-C₄H₇)(μ-C₅H₅)(PPh₃)₂] (C)⁸³ demonstrate that the unusual type of bridging discussed above for allyl groups or benzene in complexes (A) and (B) can be extended to the cyclopentadienyl group. Both structures are of the type (24) except that in (C) the bridging bromide is replaced by a bridging methallyl group. The Pd—Pd bond lengths are 2.609 Å and 2.679 Å for (24) and (C) respectively, which may be compared with the values of 2.686 Å and 2.58 Å reported for (A) and (B), respectively. In (24) the cyclopentadienyl ring has four C—C distances approximately equal (1.46–1.52 Å), but the bond parallel to the Pd—Pd axis is much shorter (1.33 Å) and the ring may be regarded as an allyl plus alkene group.

⁸⁰ A. Modinos and P. Woodward, *J.C.S. Dalton*, 1975, 1516, and references therein.

⁸¹ D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, and J. S. Miller, *J. Amer. Chem. Soc.*, 1975, **97**, 1961.

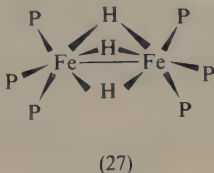
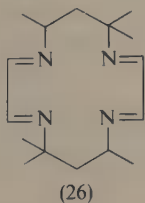
⁸² A. Ducruix, H. Felkin, C. Pascard, and C. K. Turner, *J.C.S. Chem. Comm.*, 1975, 615.

⁸³ H. Werner, D. Tune, G. Parker, C. Krüger, and D. J. Brauer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 185.

21 Metal Hydrides

Paramagnetic hydrido-complexes are still very unusual species. $[\text{ReHX}_2(\text{PPh}_3)_2(\text{acac})]$ ($\text{X} = \text{Cl}$ or I) has been isolated from reaction of $[\text{ReH}_2(\text{PPh}_3)_3(\text{acac})]$ with CCl_4 or I_2 , and several salts of the type $[\text{CoHL}_4]\text{X}$ [$\text{L} = \text{P}(\text{OEt})_2\text{Ph}$, $\text{P}(\text{OMe})_2\text{Ph}$, or $\text{P}(\text{OPh})_3$; $\text{X} = \text{PF}_6$ or BF_4] have been obtained by reaction of trityl salts with CoHL_4 . Details of the preparation and characterization of the first paramagnetic hydrides of Fe^{I} and Fe^{III} have now been reported.⁸⁴ Mild oxidation of $[\text{FeHCl}(\text{diphos})_2]$ ($\text{diphos} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) with AgClO_4 or a trityl salt yields $[\text{FeHCl}(\text{diphos})_2]\text{X}$ ($\text{X} = \text{ClO}_4$ or BF_4), and reduction of the same substrate by powdered sodium in benzene gives $[\text{FeH}(\text{diphos})_2]$. The Fe^{I} species may also be obtained by a similar reduction of $[\text{FeH}(\text{diphos})_2]\text{BPh}_4$. The Fe^{I} and Fe^{III} species have magnetic moments 1.8 and 2.16 BM, respectively, consistent with a low-spin configuration and a single unpaired electron, as found in the $[\text{CoHL}_4]^+$ ions. Presence of hydride is confirmed by evolution of hydrogen in reactions with HCl and by oxidation and reduction reactions to known Fe^{II} hydride complexes. Although they deteriorate rapidly in solution, the new hydride complexes are stable to air for several hours in the solid state and are thus considerably more stable than the $[\text{CoHL}_4]^+$ salts.⁸⁴ Although Fe^{I} is a well-established oxidation state in organometallic complexes such as $[\text{Fe}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2]$, it is still rare in derivatives of nitrogen and oxygen donors. The macrocyclic ligand (26) forms iron complexes which can be reduced by controlled-potential electrolysis to purple Fe^{I} derivatives.⁸⁵ Electrolysis in MeCN solution on the first reduction plateau (-1.2 V) gives $[\text{Fe}^{\text{I}}(\text{tetraene-N}_4)]^+$ [$\text{tetraene-N}_4 = (26)$], isolated as its $[\text{CF}_3\text{SO}_3]^-$ salt, and repeated scanning of the second reduction plateau (-1.6 V) gives $[\text{Fe}^{\text{I}}\text{H}(\text{tetraene-N}_4)(\text{MeCN})]$, $\nu(\text{Fe-H}) = 1890\text{ cm}^{-1}$, via hydrogen abstraction from the supporting electrolyte, $\text{Bu}^n_4\text{NBF}_4$; reaction with CCl_4 yields CHCl_3 . In addition to this unusual hydride, stable alkyl or aryl derivatives of Fe^{I} are isolated by reduction of $[\text{Fe}^{\text{II}}(\text{tetraene-N}_4)\text{Cl}]^+$ by lithium alkyls or aryls to yield $[\text{FeR}(\text{tetraene-N}_4)]$, $\text{R} = \text{Me}$ or Ph . All of these Fe^{I} species have magnetic moments 2.1–2.3 BM and their e.s.r. spectra are typical of low-spin d^7 systems.⁸⁵

A hydrido-complex of Fe^{I} is also formed when FeCl_2 is reduced by NaBH_4 in butan-1-ol in the presence of the triphosphine ligand $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ (P_3). Addition of $[\text{Bu}^n_4\text{N}]\text{PF}_6$ permits isolation of the complex $[\text{Fe}_2\text{H}_3(\text{P}_3)_2]\text{PF}_6$ which has been studied by X -ray diffraction on the CH_2Cl_2 solvate. The structure is as shown in (27)

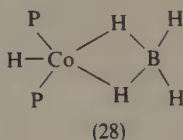


⁸⁴ M. Gargano, P. Giannoccaro, M. Rossi, G. Vasapollo, and A. Sacco, *J.C.S. Dalton*, 1975, 9, and references therein.

⁸⁵ M. C. Rakowski and D. H. Busch, *J. Amer. Chem. Soc.*, 1975, **97**, 2570.

and differs from the Fe^I species discussed above in being diamagnetic due to a metal-metal interaction.⁸⁶ The other interesting structural feature is the trihydrido bridge; only two examples seem to have been reported previously, namely $[\text{Ir}_2\text{H}_3(\eta^5\text{-C}_5\text{H}_5)_2]^+$ and $[\text{Re}_2\text{H}_3(\text{CO})_6]^-$.⁸⁷ The product of reaction of $\text{Co}(\text{BF}_4)_2$ with the arsenic analogue (A_3) of P_3 under similar conditions has also been studied by X-ray diffraction. $[\text{Co}_2\text{H}_3(\text{A}_3)_2]\text{BPh}_4$ has the same structure as (27) but is paramagnetic with $\mu_{\text{eff}} = 3.17$ BM for the dimeric entity. The metal-metal bond lengths are very similar ($\text{Fe}-\text{Fe} = 2.332 \text{ \AA}$ and $\text{Co}-\text{Co} = 2.377 \text{ \AA}$) and unusually short. Both this fact and the magnetic differences can be rationalized using an MO scheme proposed previously for confacial bioctahedral complexes. This predicts a bond order of three for the Fe complex and two for the Co complex with two unpaired electrons in degenerate anti-bonding orbitals in the latter case.⁸⁶

The bulky ligand tricyclohexylphosphine has been used to stabilize a number of unusual hydrido species. An addition this year is the paramagnetic hydride, $[\text{CoH}(\text{BH}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$, formed by reaction of CoCl_2 and $\text{P}(\text{C}_6\text{H}_{11})_3$ with NaBH_4 in toluene-ethanol solution. Magnetic susceptibility ($\mu_{\text{eff}} = 2.15$ BM) and e.s.r. measurements are typical of low-spin Co^{II} , with $\nu(\text{Co}-\text{H}) = 1797 \text{ cm}^{-1}$. X-Ray diffraction shows structure (28) with co-ordinated BH_4 completing a distorted square-pyramidal geometry about cobalt. The $\text{Co}-\text{H}$ length (1.34 \AA) appears unusually short but this conclusion is tentative in view of the high standard deviation (0.09 \AA). The complex is an active catalyst for hydrogenation and isomerization of olefins.⁸⁸



22 Organometallic Compounds

One-carbon Ligands.—*Alkyls* (see ref. 16a). A brief report suggests that reaction of manganese(II) chloride with a trimethylsilylmethyl-metal derivative or a related reagent gives the crystalline alkyls $\text{Mn}(\text{CH}_2\text{R})_2$ ($\text{R} \equiv \text{SiMe}_3$, CMe_3 , or CMe_2Ph), which are thermally stable to over 100°C , in contrast to the ready detonation of MnMe_2 , the only previously known binary alkyl for this oxidation state. Oxidation of the new alkyls by molecular oxygen gives green products which may be $\text{Mn}(\text{CH}_2\text{R})_4$ species, analogous to the tetranorbornyl Mn^{IV} compounds reported previously. Lithium salts of the alkylate anions $[\text{MnMe}_4]^{2-}$, $[\text{CoR}_4]^{2-}$ ($\text{R} = \text{Me}$ or CH_2SiMe_3), and $[\text{U}(\text{CH}_2\text{SiMe}_3)_6]^{2-}$ have also been obtained.⁸⁹ Alkyls of rhenium are even more difficult to obtain than those of manganese, except of course for carbonyls and

⁸⁶ P. Dapporto, S. Midollini, and L. Sacconi, *Inorg. Chem.*, 1975, **14**, 1643.

⁸⁷ C. White, A. J. Oliver, and P. M. Maitlis, *J.C.S. Dalton*, 1973, 1901, and references therein.

⁸⁸ M. Nakajima, H. Moriyama, A. Kobayashi, T. Saito, and Y. Sasaki, *J.C.S. Chem. Comm.*, 1975, 80.

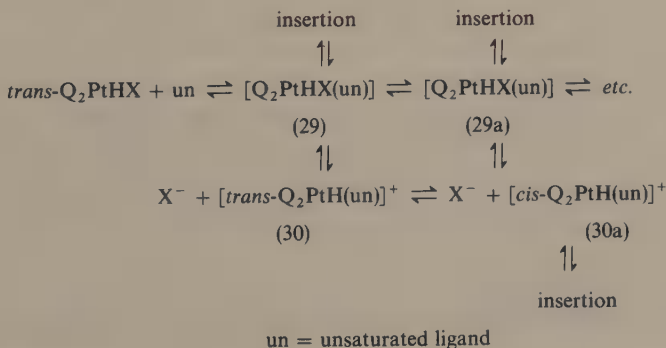
⁸⁹ R. Andersen, E. Carmona-Guzman, K. Mertis, E. Sigurdson, and G. Wilkinson, *J. Organometallic Chem.*, 1975, **99**, C19.

related species. $[\text{ReOMe}_4]$ was reported only last year and the full papers have now been published.⁹⁰ Reactions of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ or $[\text{ReOCl}_4]$ with LiMe in diethyl ether both give $[\text{ReOMe}_4]$, the former in 70% and the latter in 20% yield. In the former case, traces of O_2 are necessary for high yields; O_2 does not affect the yield in the latter reaction but it is evident that both processes are more complex than simple methylation. $[\text{ReO}(\text{CH}_2\text{SiMe}_3)_4]$ and $[\text{Re}_2\text{O}_3(\text{CH}_2\text{SiMe}_3)_6]$ have also been prepared by reaction of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ with $[\text{ReOCl}_3(\text{PPh}_3)_2]$; the former is air stable in contrast to $[\text{ReOMe}_4]$. Both oxotetra-alkyl species are paramagnetic and e.s.r., electronic absorption, and i.r. spectra are consistent with a square-pyramidal structure.⁹⁰ WMe_6 was first prepared in 1972 and, as reported last year, TaMe_5 is (with ReMe_6 , *vide infra*) the only other example of a homoleptic methyl in an oxidation state greater than four. Preparation of WMe_6 by interaction of LiMe and WCl_6 is a rather complex reaction, and it now appears that some of the difficulties are due to the fact that adventitious oxygen is required.⁹¹ Reaction of WCl_6 with trimethylaluminium at -70°C is a better procedure for preparing WMe_6 , and it is important to note that the compound is potentially explosive. The analogous reaction of AlEt_3 with $[\text{ReOMe}_4]$ yields the new, green, paramagnetic ReMe_6 , which is reasonably stable at 25°C . A stable methyl of an even higher oxidation state, $[\text{Re}^{\text{VII}}\text{O}_2\text{Me}_3]$, is obtained by oxidation of $[\text{ReOMe}_4]$ with nitric oxide,⁹¹ a reaction which must finally dispel the idea that alkyls are stabilized only in low oxidation states.

Insertion Reactions.—The importance of the β -hydride elimination process as a factor in destabilizing transition-metal alkyl complexes has been noted.^{16a} There is still very little information available on the intimate mechanism of the reaction but the reverse process, hydride insertion, has been studied in more detail, especially for platinum complexes. For the general reaction (30) two principal mechanisms have



been discussed, and a paper this year⁹² summarizes the existing data and proposes a unified reaction scheme (Scheme 7). Originally, the reaction was assumed to involve

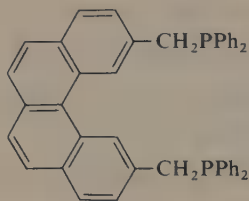


Scheme 7

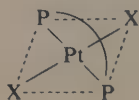
⁹⁰ K. Mertis, D. H. Williamson, and G. Wilkinson, *J.C.S. Dalton*, 1975, 607; J. F. Gibson, K. Mertis, and G. Wilkinson, *J.C.S. Dalton*, 1975, 1093.

⁹¹ L. Galyer, K. Mertis, and G. Wilkinson, *J. Organometallic Chem.*, 1975, **88**, C37.

associative alkene co-ordination to give a five-co-ordinate intermediate (29) followed by rearrangement to the square-planar insertion product. Complexes similar to (29) have been isolated, *e.g.* $[\text{PtH}(\text{CN})\{\text{C}_2(\text{CN})_4\}(\text{PET}_3)_2]$ and $[\text{PtClMe}\{\text{C}_2(\text{CF}_3)_2\}(\text{AsMe}_2\text{Ph})]$, but only the methyl complex has been shown to undergo a subsequent insertion reaction. Recent kinetic data have tended to favour four-co-ordinate intermediates (30), and *trans*- $[\text{PtH}(\text{C}_2\text{H}_4)(\text{PET}_3)_2]^+$ has been observed by n.m.r. spectroscopy in the reaction of *trans*- $[\text{PtH}(\text{acetone})(\text{PET}_3)_2]^+$ with C_2H_4 and isolated as its $[\text{BPh}_4]^-$ salt from the reaction of *trans*- $[\text{PtH}(\text{NO}_3)(\text{PET}_3)_2]^+$ with C_2H_4 . In the unified reaction Scheme 7, the five-co-ordinate intermediate (29) may be either a transition state or a *bona fide* intermediate. Weak ligands (NO_3^- , acetone, MeOH , *etc.*) favour (30) [*i.e.* (29) is then a transition state] and stronger ligands (29), although in the latter case definition of the necessary ligand properties is not clear-cut. The intermediates (29a) and (30a) represent changes of stereochemistry which may be necessary before insertion can occur.⁹² For (29) this presents little difficulty since stereochemical interchange is facile in five-co-ordinate systems but in (30) there is a problem presented by the observed *trans* geometry of the intermediates and the necessity for adjacent hydride and C_2H_4 positions prior to insertion. This could be resolved either by an X^- -assisted *trans* \rightarrow *cis* isomerization (Scheme 7) or by an associative process involving an additional C_2H_4 molecule.⁹³ The *trans* \rightarrow *cis* isomerization route is suggested by the analogous reaction of *trans*- $[\text{PtHX}(\text{PET}_3)_2]$ with alkynes, which always results in a vinyl with Pt and H in mutually *cis* positions.⁹⁴ However, this mechanism is clearly not possible for ethylene insertion into the Pt—H bond of *trans*- $[\text{PtHCl}(\text{P—P})]$, where P—P is the diphosphine (31), which spans *trans* positions in square-planar complexes (32).⁹⁵ The problem has also been discussed regarding the insertion



(31)



(32)

reactions of *trans*- $[\text{PtMe}(\eta\text{-allene})(\text{PMe}_2\text{Ph})_2]^+$ to *cis*- $[\text{Pt}(\eta\text{-2-methylallyl})(\text{PMe}_2\text{Ph})_2]^+$. The relation to the above insertions is clear and the reaction shows first-order kinetics. A five-co-ordinate transition state is considered unlikely since addition of anionic or neutral donors or excess allene suppresses the insertion. A slight dependence of ΔH^\ddagger on the counter-ion, $\text{SbF}_6^- \sim \text{BF}_4^- > \text{PF}_6^-$, suggests that the reactive species is a tight ion pair, but it seems that the chief role of cationic intermediates in promoting Pt—H and Pt—C insertions is activation of the unsaturated hydrocarbon rather than stabilization of five-co-ordinate intermediates.⁹⁶ The

⁹² H. C. Clark, C. R. Jablonski, and C. W. Wong, *Inorg. Chem.*, 1975, **14**, 1332, and references therein.

⁹³ H. C. Clark, C. R. Jablonski, J. Halpern, A. Mantovani, and T. A. Weil, *Inorg. Chem.*, 1974, **13**, 1541.

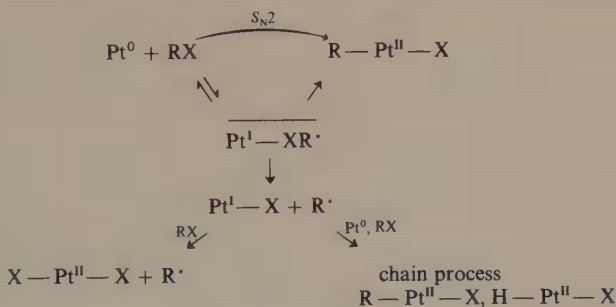
⁹⁴ H. C. Clark and C. S. Wong, *J. Organometallic Chem.*, 1975, **92**, C31.

⁹⁵ G. Bracher, P. S. Pregosin, and L. M. Venanzi, *Angew. Chem. Internat. Edn.*, 1975, **14**, 563.

⁹⁶ M. H. Chisholm and W. S. Johns, *Inorg. Chem.*, 1975, **14**, 1189.

possibility of achieving adjacent hydride and ethylene positions *via* tetrahedral intermediates remains essentially unexplored.

Oxidative Addition.—This is another reaction of central importance in organometallic mechanisms.⁹⁷ As reported last year, use of the spin trap Bu'NO has provided evidence for a non-chain radical process in the oxidative addition of alkyl halides to [Pt(PPh₃)₃] and stereochemical studies on similar reactions of [Pd(PPh₃)₃] have suggested an S_N2 type of attack by the metal at the carbon centre. The latter work also indicated a need for caution in that addition of Bu'NO to the reaction of PhMeCHBr with [Pd(PPh₃)₄] produced Bu'(PhCH₂)NO•, even though the reaction probably does not normally proceed by a radical mechanism (this is because Pd^{II} alkyls are significantly less stable than Pt^{II} analogues and react with Bu'NO). However, CIDNP evidence has now confirmed that radicals are involved in oxidative



Scheme 8

addition of isopropyl iodide to [Pt(PEt₃)₃]. Moreover, this reaction, in common with several others involving reactive alkyl halides, is more complex than a simple addition to form *trans*-[Pt(Pr')I(PEt₃)₂]; other products are *trans*-[PtHI(PEt₃)₂], *trans*-[PtI₂(PEt₃)₂], propene, propane, and 2,3-dimethylbutane. Scheme 8 is proposed to unify these and other observations. The initially formed radical pair (Pt^I—X, R•) can collapse to the regular adduct or diffusively separate. Subsequent reaction of the separated radicals depends on the reactivity of the alkyl halide; very reactive ones form dihalide and organic radicals and less reactive ones initiate a chain process.⁹⁷ The initial radical pair formation may be preceded by one-electron transfer. The reaction of M(PEt₃)₃ (M = Pt or Ni) with tetracyanoethylene (TCNE) generates the TCNE radical anion, detected by e.s.r., but the corresponding M^I species is not observed.⁹⁸ In contrast, reductive elimination reactions in two cases studied this year appear to occur by concerted intramolecular processes. Thermolysis of *cis*-[PtAr₂L₂] {Ar = Ph or 4-MeC₆H₄, L₂ = (PPh₃)₂, [P(4-MeC₆H₄)₃]₂, Ph₂PC₂H₄PPh₂, or Ph₂PCH₂PPh₂} generated Ar₂ quantitatively and without isomerization, whereas radical pathways or *ortho*-metallation should produce ArH or isomerized aryls.⁹⁹ Moreover, kinetic studies on reductive elimination of ethane

⁹⁷ A. V. Kramer and J. A. Osborn, *J. Amer. Chem. Soc.*, 1974, **96**, 7832, and references therein.

⁹⁸ I. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organometallic Chem.*, 1975, **84**, C7.

⁹⁹ P. S. Braterman, R. J. Cross, and G. B. Young, *J.C.S. Chem. Comm.*, 1975, 627.

from *fac*-[PtClMe₃(PMe₂Ph)₂] suggest a concerted elimination process from a five-co-ordinate intermediate formed by dissociation of tertiary phosphine. The intermediate resembles an ethane complex of platinum(II) and the process is similar to that previously proposed for reductive elimination from Au^{III} species.¹⁰⁰

Dialkylaminomethyl and Dialkylphosphinomethyl Ligands.—The ligating properties of unsaturated species containing heteroatoms are a potentially rich field of chemistry. A structure containing η^2 -bonded [Me₂N=CH₂]⁺, a formal three-electron donor, was first suggested in 1971 for the complex [CuCl(Me₂NCH₂)]Br. This type of co-ordination has been confirmed by X-ray study of (CH₂CH₂NCH₂)Mn(CO)₅, which has Mn—N = 1.98 Å, Mn—C = 2.09 Å, and C—N = 1.45 Å, the last being an essentially typical single bond length. A wide range of (η^2 -R₂CNHR)₂M(CO)₄ (M = Mn or Re) complexes has now been reported from elimination of R₃SnBr between R₂NCH₂SnR₃¹ and M(CO)₅Br.¹⁰¹ A more direct approach¹⁰² uses reaction of [Me₂NCH₂]I with Na[M(CO)₃(η^5 -C₅H₅)] (M = Mo or W) to synthesize the σ -bonded derivatives M(CO)₃(η^5 -C₅H₅)(η^1 -CH₂NMe₂). When M = Mo, the σ -bonded complex transforms under reflux in light petrol to the π -bonded derivative, Mo(CO)₂(η^5 -C₅H₅)(η^2 -CH₂NMe₂), a reaction reminiscent of the familiar $\sigma \rightarrow \pi$ allyl interchange. The change is from one- to three-electron donor in both cases. Curiously, the expected magnetic inequivalence of N-methyl groups and methylene protons is not observed in the n.m.r. spectrum and this situation is also found for the seven-co-ordinate derivatives, M(CO)₃(NCMe)(η^2 -CH₂NMe₂), obtained by reaction of [Me₂NCH₂]I with M(CO)₃(NCMe)₃. In addition to the η^1 and η^2 derivatives, an unusual reaction of [Me₂NCH₂]I with [Fe(CO)₄]²⁻ or [Cr(CO)₅]²⁻ yields the known carbene complexes Fe(CO)₄(CHNMe₂) and Cr(CO)₅(CHNMe₂), presumably by hydrogen abstraction from one MCH₂NMe₂ group to give NMe₃.¹⁰²

Analogous phosphino-derivatives have also been reported.¹⁰³ Reaction of CoCl(PMe₃)₃ with the ylide Me₃PCH₂ gives a very air-sensitive red product formulated as Co(η^2 -CH₂PMe₂)(PMe₃)₃ on the basis of ¹H and ³¹P n.m.r. Interestingly, in view of the above observations on η^2 -CH₂NMe₂, the compound is fluxional and assignment of definite phosphorus positions in the co-ordination sphere is not possible. The η^2 -CH₂PMe₂ system can also arise by an unusual oxidative addition reaction. Treatment of FeCl₂(PMe₃)₂ with Mg and PMe₃ in THF yields FeH(η^2 -CH₂PMe₂)(PMe₃)₃ from oxidative addition of a trimethylphosphine to the Fe centre. It is suggested that equilibrium formation of Fe(PMe₃)₄ may be involved in reactions of this species.¹⁰³ X-Ray confirmation of the η^2 -CR₂PR₂ possibility has come from a rather unexpected quarter. *trans*-[PtCl₂(PPrⁿ)₂] reacts with 1-lithium 2-phenyl-1,2-dicarbasododecaborane to give a product containing a σ -carbaboranyl ligand and an internally metallated η^2 -P(Prⁿ)₂CH₂Et ligand (cited in ref. 103).

Two Carbon Ligands.—*Aza-allyl Complexes and Related Species.* Continuing the theme of ligating properties of hetero-unsaturated ligands, we note that 2-aza-allyl

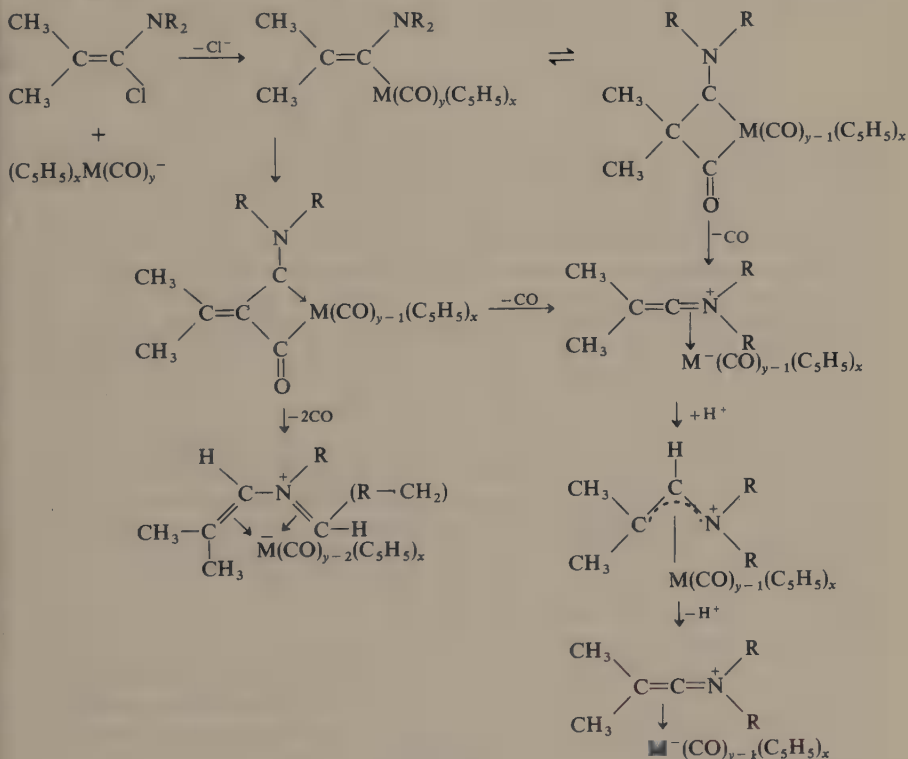
¹⁰⁰ M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1974, 2457.

¹⁰¹ E. W. Abel and R. J. Rowley, *J.C.S. Dalton*, 1975, 1096, and references therein.

¹⁰² C. W. Fong and G. Wilkinson, *J.C.S. Dalton*, 1975, 1100.

¹⁰³ H. H. Karsch, H. F. Klein, and H. Schmidbaur, *Angew. Chem. Internat. Edn.*, 1975, **14**, 637, and references therein.

complexes have been known for several years. An unusual reaction of LiNCR_2 ($\text{R} = \text{Ph}$ or *p*-tolyl) with $\text{MCl}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Mo}$ or W) yields $\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)(\text{R}_2\text{CNCR}_2)$ complexes by elimination of cyanate. An X-ray study of the complex with $\text{M} = \text{Mo}$ and $\text{R} = p\text{-tolyl}$ shows a bent (128°) aza-allene structure with the CR_2 planes mutually perpendicular, but low-temperature n.m.r. studies suggest an asymmetric π -aza-allyl structure in solution.¹⁰⁴ Extension of this work to 1,3-diaza-allyl compounds has been achieved by reactions of $\text{RNC}(\text{R})\text{NRLi}$ with $\text{MCl}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ or with $\text{MnX}(\text{CO})_5$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$). In the latter case, the initial product is a carbamoyl complex, $\text{Mn}(\text{CO})_4\{\text{CO}\cdot\text{NR}\cdot\text{C}(\text{R})=\text{NR}\}$, which decarboxylates under u.v. irradiation to $\text{Mn}(\text{CO})_4\{\text{RN}\cdot\text{C}(\text{R})=\text{NR}\}$. Co-ordination of the hetero-ligand is probably of a σ, σ -type analogous to a carboxylate rather than an allyl group.¹⁰⁴ Reactions of an α -chloroenamine, $\text{Me}_2\text{C}=\text{C}(\text{NR}_2)\text{Cl}$ [$\text{R} = \text{Me}$ or



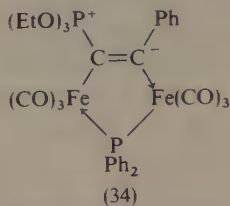
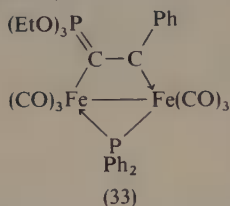
Scheme 9

$2\text{R} = (\text{CH}_2)_5]$ with \blacksquare carbonyl anion $[\text{M}(\text{CO})_5]^-$ ($\text{M} = \text{Mn}$ or Re), $[\text{M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]^-$ ($\text{M} = \text{Mo}$ or W), $[\text{Co}(\text{CO})_4]^-$, or $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]^-$ reveal an exceptionally varied co-ordination chemistry (Scheme 9). Seven different modes of co-ordination are established by spectroscopic data including the first examples of 1-aza-allyl and 2-azabutadiene complexes, the former being an Mo species isolated as

¹⁰⁴ T. Inglis and M. Kilner, *J.C.S. Dalton*, 1975, 924, 930, and references therein.

its PF_6^- salt and the latter an Mn compound formed by hydrogen migration in the ligand system.¹⁰⁵

Phosphonium Betaine Complexes. (See also Section 13.) Reaction of (21) with triethyl phosphite results in nucleophilic attack at the α -carbon of the acetylide to yield a new type of two-carbon three-electron ligand. X-Ray diffraction studies of the product, $\text{Fe}_2(\text{PPh}_2)(\text{CO})_6\text{C}\{\text{P}(\text{OEt})_3\}\text{CPh}$, show a structure with C—C and P—C bond lengths in the bridging group 1.34 and 1.74 Å, respectively. This indicates considerable multiple character in both bonds and a formulation intermediate between (33) and (34).¹⁰⁶



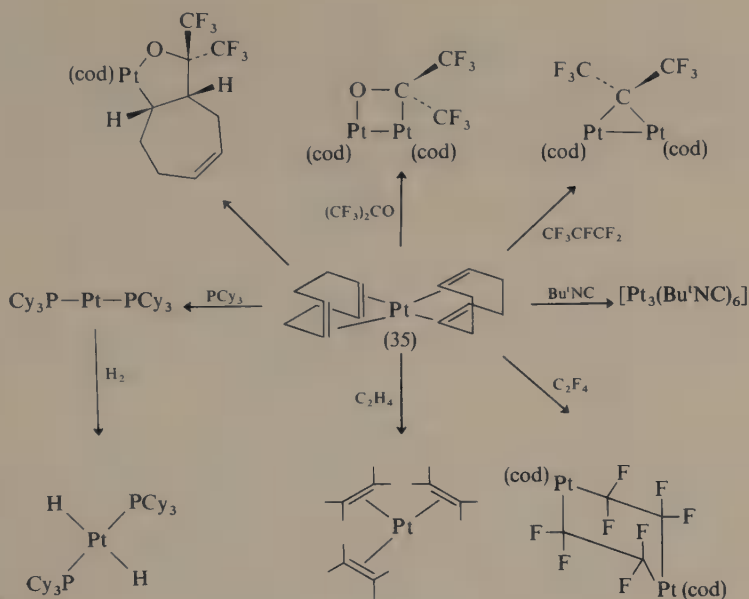
Tris(ethylene)platinum and Related Species. The synthetic potential and catalytic activity of labile olefin-substituted M^0 complexes are well established. The many elegant studies using bis(cyclo-octa-1,5-diene)nickel and cyclo-dodeca-1,5,9-trienenickel are of particular interest, and the tremendous potential of corresponding platinum complexes is obvious. Although bis(cyclo-octa-1,5-diene)platinum (35) has been obtained previously by u.v. irradiation of $\text{PtPr}_2^i(1,5\text{-C}_8\text{H}_{12})$ in the presence of $1,5\text{-C}_8\text{H}_{12}$, a convenient and reliable synthesis was lacking. Moreover, the other known Pt^0 species, such as $\text{Pt}(\text{PPh}_3)_3$ or $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ contain relatively non-labile tertiary phosphines. Thus the preparation of (35) in good yield by the treatment of $\text{Li}_2\text{C}_8\text{H}_8$ with $\text{PtCl}_2(1,5\text{-C}_8\text{H}_{12})$ in the presence of excess $1,5\text{-C}_8\text{H}_{12}$ is an important advance and has already led to much novel chemistry (Scheme 10).¹⁰⁷ The structure of $\text{Pt}(\text{C}_2\text{H}_4)_3$ and related species is of especial interest since a theoretical study of $\text{Ni}(\text{C}_2\text{H}_4)_3$ has predicted a trigonal-planar structure rather than one having alkene ligands perpendicular to the co-ordination plane. The only X-ray structure confirming this prediction was that of tris(bicyclo[2,2,1]heptene)nickel. This type of structure has now been confirmed for $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{F}_4)$, easily derived from $\text{Pt}(\text{C}_2\text{H}_4)_3$ by a simple displacement reaction, and also for tris(bicyclo[2,2,1]heptene)palladium (D) and the corresponding platinum compound and $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)$. The last example was characterized by ^{13}C n.m.r. studies (the others by X-ray diffraction) which show rotation of the co-ordinated ethylene at ambient temperature and a trigonal-planar structure at low temperatures. Bis(cyclo-octa-1,5-diene)palladium (E) has also been obtained by a reaction analogous to the synthesis of (35), and reacts with C_2H_4 to produce a complex which is probably $\text{Pd}(\text{C}_2\text{H}_4)_3$.¹⁰⁷ Preparation of (D) and (E) on a gram scale has also been achieved by condensation of palladium atoms with the appropriate ligand at low temperatures (-196 and -120°C , respectively).¹⁰⁸

¹⁰⁵ R. B. King and K. C. Hodges, *J. Amer. Chem. Soc.*, 1975, **97**, 2702.

¹⁰⁶ Y. S. Wong, H. N. Paik, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1975, 309.

¹⁰⁷ M. Green, J. A. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 3, 449; M. Green, J. A. K. Howard, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 451, and references therein.

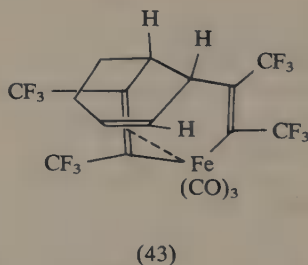
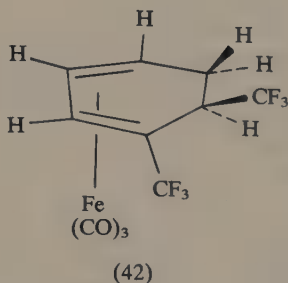
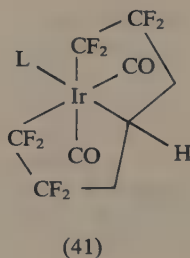
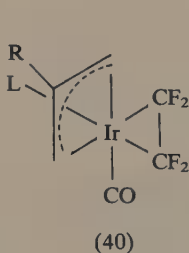
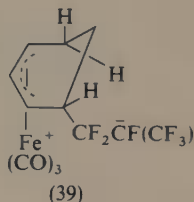
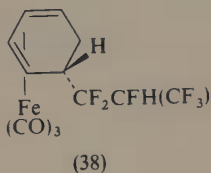
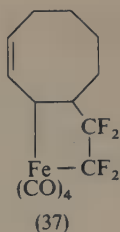
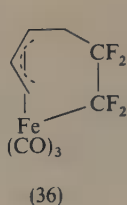
¹⁰⁸ R. M. Atkins, R. MacKenzie, P. L. Timms, and T. W. Turney, *J.C.S. Chem. Comm.*, 1975, 764.



Scheme 10

Formation and Cleavage of C—C Bonds ■ Metal Sites.—Linking reactions of unsaturated substrates at metal centres are of obvious importance in understanding many organometallic processes, but established general reaction classes are relatively rare. A common approach is to utilize fluorocarbon species since this frequently stabilizes reactive intermediates. During the past several years, oxidative linking such as the reaction of tricarbonyl(butadiene)iron with C_2F_4 to yield (36), has been shown to be a fairly general reaction. A series of papers published this year¹⁰⁹ shows that several other types of product are also obtained. Thus tricarbonyl(cycloocta-1,3-diene)iron with C_2F_4 gives the ferracyclopentane (37) in addition to the expected product, and tricarbonyl(cyclohexa-1,3-diene)iron with CF_2CFCF_3 gives (38), in addition to products related to (36) and (37). Compound (37) is regarded as derived from the initial π -allylic insertion product by $\pi \rightarrow \sigma$ allyl interchange. Isolation of (38), together with results on the stereochemistry and position of linking in substituted dienes and fluoro-olefins, suggests that the mechanism of the reaction is *via endo* attack by olefin on the diene to give an ionic intermediate such as (39). The alternative reaction path *via* initial attack of fluoro-olefin on Fe cannot be excluded in some cases. Reactions essentially similar to the formation of (36) also occur between $\text{M}(1,3\text{-diene})(\text{CO})_3$ ($\text{M} = \text{Fe}$ or Ru) and hexafluoroacetone and between $\text{Ir}(\eta^3\text{-RC}_3\text{H}_4)(\text{CO})\text{L}_2$ ($\text{L} = \text{PPh}_3$ or AsPh_3) and C_2F_4 or $\text{CF}_3\text{C}\equiv\text{CCF}_3$. In the $\text{Ir}-\text{C}_2\text{F}_4$ case, an initial adduct (40) is isolated, and the linking reaction involves a second C_2F_4 molecule which forms $[\text{CH}_2=\text{CRCH}_2\text{CF}_2\text{CF}_2\text{Ir}(\eta^2\text{-C}_2\text{F}_4)(\text{CO})\text{L}]$ when $\text{R} = \text{Me}$. However, when $\text{R} = \text{H}$ the unusual iridocycle (41) results.¹⁰⁹

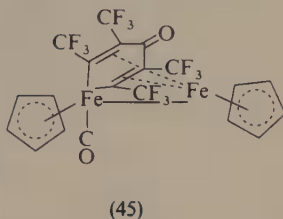
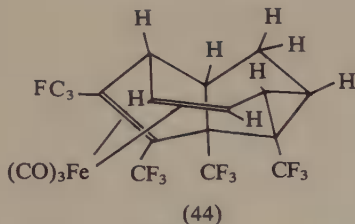
¹⁰⁹ M. Bottrill, R. Goddard, M. Green, R. P. Hughes, M. K. Lloyd, S. H. Taylor, and P. Woodward, *J.C.S. Dalton*, 1975, 1150; see also preceding papers in this series and references therein.



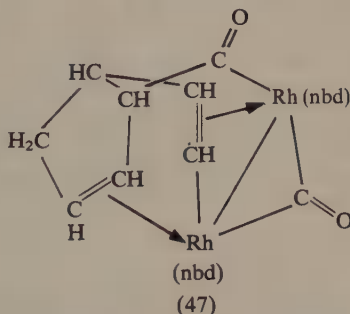
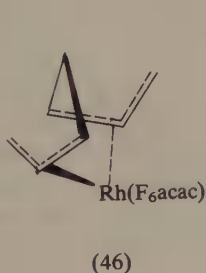
Extension of this work¹¹⁰ to reactions of hexafluorobut-2-yne (HFB) with tricarbonyl(butadiene)iron yields an insertion product analogous to (36) and thermolysis of this product under reflux in hexane gives (42). This overall reaction involves stepwise Diels-Alder addition of HFB to co-ordinated buta-1,3-diene, a result which suggests that previously reported examples of concerted 'forbidden' reactions at transition metals may also have stepwise mechanisms. HFB and tricarbonyl-

¹¹⁰ M. Bottrill, R. Goddard, M. Green, R. P. Hughes, M. K. Lloyd, B. Lewis, and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 253; J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *ibid.*, p. 286; R. Davis, M. Green, and R. P. Hughes, *ibid.*, p. 405.

(cyclohexa-1,3-diene)iron give the double insertion product (43), but with tricarbonyl(cycloheptatriene)iron a remarkable addition of two molecules of CF_3CCCF_3 occurs on the *endo* face of the triene to yield the quadricyclic ligand complex, (44). Another unusual product is (45) {obtained by reaction of HFB with $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$ }, a type of intermediate which has been frequently postulated in metal-catalysed formation of cyclopentadienones and quinones.¹¹⁰



Another important class of reaction is transition-metal cleavage of C—C bonds of cyclic ligands. The classic example here is insertion of Pt^{IV} into cyclopropane ring systems, and X-ray studies have established that a C—C bond is cleaved even though cyclopropane can be displaced by several donor ligands.¹¹¹ An interesting addition this year is the cleavage of *trans*-divinylcyclopropane by bis(ethylene)hexafluoroacetylacetonatorhodium(I) to give the bis(allyl) complex (46).¹¹² However, examples for ring systems other than cyclopropane are still rare and the following are therefore of interest. In each case products have been characterized by X-ray diffraction. The final product from reaction of norbornadiene (nbd) with $\text{Rh}_6(\text{CO})_{16}$ is (47), derived from ring-opening of nbd and possibly a stabilized retro-Diels–Alder intermediate.¹¹³ Low-temperature n.m.r. spectra of $\{\text{endo}-(\text{RO})\text{C}_4\text{Ar}_4\}\text{Pd}(\text{acac})$,



$\text{R} = \text{Me}$ or Et , $\text{Ar} = \text{Ph}$ or $p\text{-FC}_6\text{H}_4$, demonstrate that the ring-closing step in the formation of cyclobutenyl derivatives from PhCCPh and PdCl_2 in alcohols is readily reversible. Isomers (48) and (49) are both present in the solution.¹¹⁴ Reversible opening of a saturated C_4 ring has been demonstrated in the conversion of (50) into (51). Both compounds contain two of the illustrated structural units joined by chloride bridges. The *endo*-phenyl analogue of (51) is present during the reaction

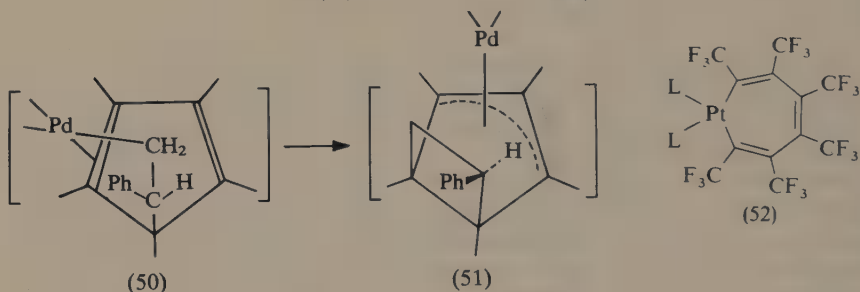
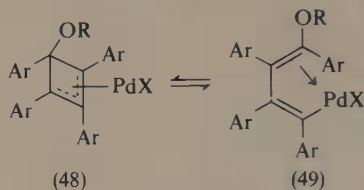
¹¹¹ R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organometallic Chem.*, 1971, **33**, 247.

¹¹² N. W. Alcock, J. M. Brown, J. A. Conneely, and J. J. Stofko, jun., *J.C.S. Chem. Comm.*, 1975, 234.

¹¹³ J. A. J. Jarvis and R. Whyman, *J.C.S. Chem. Comm.*, 1975, 562.

¹¹⁴ P. T. Cheng, T. R. Jack, C. J. May, S. C. Nyburg, and J. Powell, *J.C.S. Chem. Comm.*, 1975, 369.

and has been isolated, thus demonstrating that the ring-closure is readily reversible.¹¹⁵ Finally, perhaps the most unusual of all is the insertion of Pt^0 into an arene C—C bond. $[\text{Pt}_3(\text{Bu}'\text{NC})_6]$ or *trans*-stilbenebis(trimethylphosphine)platinum reacts with hexakis(trifluoromethyl)benzene to give (52; $\text{L} = \text{Bu}'\text{NC}$ or PMe_3), which represents a new type of possible intermediate in cyclo-oligomerization reactions of alkynes.¹¹⁶



23 Catalytic Processes

The 'heterogenizing' of homogeneous catalytic systems is an area of developing interest and has been reviewed recently.¹¹⁷ The objective of this research is to combine the ease of recovery of a heterogeneous catalytic system with the great activity, selectivity, and ease of mechanistic study of a homogeneous system. The most usual approach uses polystyrene, cross-linked with divinylbenzene, as a polymer support and ligating groups are introduced by substitution on the polymer chain. Papers published this year¹¹⁸ provide a thorough investigation of a number of typical systems and describe the important new possibility of anchoring more than one type of catalyst to the same polymer chain, thus enabling catalysis of sequential multistep reactions.

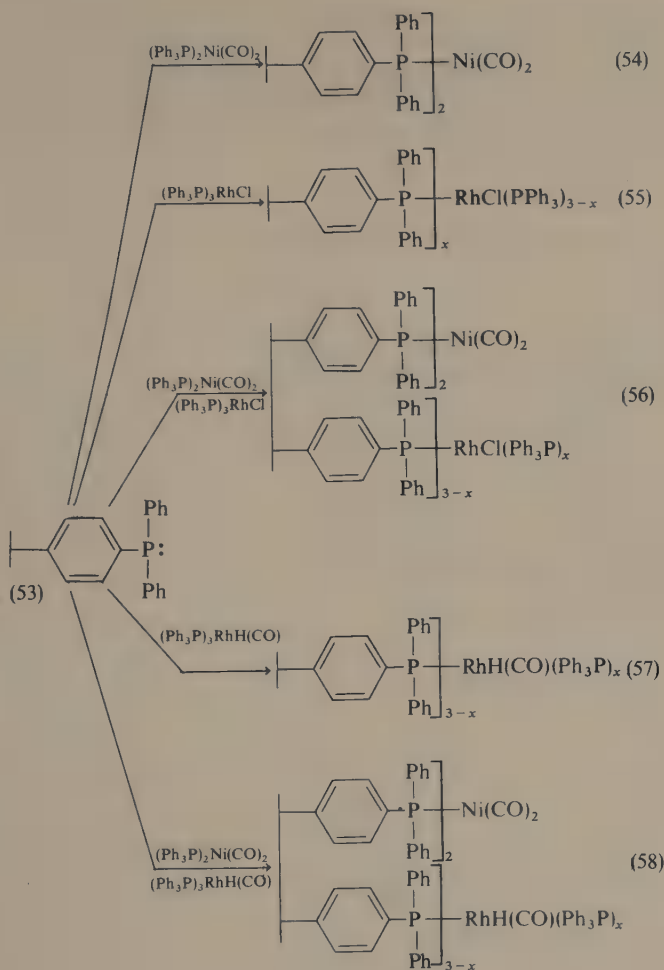
Iron-catalysed bromination of polystyrene followed by reaction with LiPPh_2 leads to the *para*- PPh_2 substituted derivative (53). Simple phosphine exchange reactions, as shown in Scheme 11, yield the appropriate transition-metal substituted polymers (54)—(58). Among the reactions studied are cyclo-oligomerization of butadiene catalysed by (54) to yield (59), (60), and (61); hydrogenation of these products catalysed by (55) to yield the fully saturated analogues of (59)—(61); and hydroformylation of (59) catalysed by (57) to yield (62) and (63). The product distributions

¹¹⁵ D. J. Mabbott, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1975, 521.

¹¹⁶ J. Browning, M. Green, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 723.

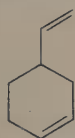
¹¹⁷ J. C. Bailar, jun., *Catalysis Rev.*, 1974, **10**, 17.

¹¹⁸ C. U. Pittman, jun., L. R. Smith, and R. M. Hanes, *J. Amer. Chem. Soc.*, 1975, **97**, 1742; C. U. Pittman, jun. and L. R. Smith, *ibid.*, p. 1749.



Scheme 11

and responses to excess PPh_3 , temperature changes, and changes in H_2 or CO pressures demonstrate the mechanistic similarity of the polymer-anchored systems to their homogeneous analogues. Rates are generally somewhat lower than those achieved with the homogeneous analogues, probably owing to diffusion retardation in the anchored catalysts.



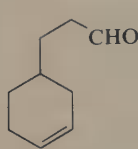
(59)



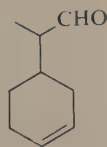
(60)



(61)



(62)



(63)

In addition to the above processes, sequential cyclo-oligomerization of butadiene to (59), (60), and (61) followed by hydrogenation to the fully saturated compounds has been achieved using the catalyst (56), thus demonstrating the possibility of constructing a single catalyst to achieve a multistep conversion in a 'one pot' process. Sequential cyclo-oligomerization of butadiene followed by hydroformylation to (62) and (63) is achieved by catalyst (58).¹¹⁸

Table 1 *Molecular structures and electronic configurations of some pentacarbonyl species*

| <i>Penta-carbonyl</i> | <i>Stereo-chemistry^a</i> | <i>No. of valence shell electrons</i> |
|----------------------------|-------------------------------------|---------------------------------------|
| $\text{V}(\text{CO})_5$ | S.P. | 15 |
| $\text{Cr}(\text{CO})_5$ | S.P. | 16 |
| $\text{Mn}(\text{CO})_5$ | S.P. | 17 |
| $\text{Cr}(\text{CO})_5^-$ | S.P. | 17 |
| $\text{Fe}(\text{CO})_5$ | T.B. | 18 |
| $\text{Mn}(\text{CO})_5^-$ | T.B. | 18 |

(a) S.P. = square-pyramidal, T.P. = trigonal-bipyramidal.

Author Index

- Abbar, C., 19
 Abel, E. W., 212
 Adams, D. M., 92
 Adams, R. D., 155
 Adedigbo, F. A., 192
 Adolphson, D. G., 123
 Agapiou, A. A., 193
 Agarwal, R. P., 178
 Agarwal, V. K., 43
 Aime, S., 203
 Akora, S. K., 195
 Albano, V. G., 205
 Alben, R., 34
 Albrand, J. P., 129
 Alcock, N. W., 126, 217
 Alder, B. J., 14, 16
 Aldrich, H. S., 115
 Alefeld, B., 41
 Alimov, I. M., 152
 Allcock, H. R., 132
 Allen, A. D., 156
 Allinger, K., 156
 Allison, S., 37
 Alt, H. G., 184
 Alyen, E. C., 173
 Amma, E. L., 195
 Andersen, R., 183, 208
 Andersen, R. A., 95
 Anderson, D. L., 163
 Anderson, R. L., 197
 Anderson, S. J., 175
 Anderson, S. P., 129, 130
 Andrews, L., 143, 144, 145, 180
 Angus, P. C., 120
 Anisimov, K. N., 198
 Anisimov, S. I., 53
 Anker, W. J., 205
 Annarelli, D. L., 187
 Antaraitis, C., 166
 Appel, R., 132
 Aranes, A., 171
 Arjomand, M., 177
 Armatis, F. J., 123
 Armitage, F., 194
 Armor, J. N., 166, 167
 Arnold, D. P., 119
 Arnold, E., 194
 Arnould-Netillard, H., 60
 Ashe, A. J., tert., 108
 Atkins, P. W., 67, 69, 70, 72, 73, 74, 77, 80, 81
 Atkins, R. M., 214
 Atkinson, L., 125
 Attig, T. G., 174
 Atwood, J. L., 184
 Auel, T., 195
 Ault, B. S., 144
 Avakian, P., 67, 80, 88
 Averill, B. A., 164, 165
 Azizov, A. A., 188
 Bacri, J. C., 56
 Baes, M. K., 69
 Baggett, N., 152
 Bailar, J. C., jun., 218
 Bailey, P. M., 218
 Bailey, R. T., 16
 Baker, E. C., 183
 Baker, W. A., 177
 Balch, A. L., 175, 178, 206
 Balducci, A., 116
 Baldwin, J. E., 163
 Ball, C., 159
 Bard, A. J., 83, 84, 85, 86, 87
 Barefield, E. K., 173, 174
 Barker, G. K., 106, 115
 Barnett, B. L., 123, 149
 Barnik, M. I., 60
 Barojas, J., 14
 Bart, J. C. J., 123
 Bartell, L. S., 129
 Bartke, T. C., 195
 Bartoli, F. J., 25
 Barton, A. F. M., 6
 Barton, J. J., 187
 Barton, T. J., 188
 Baschetto, D. J., 185
 Basmanova, S. N., 67
 Basolo, F., 160, 162, 163, 167
 Bastide, J., 108
 Bates, R. B., 195
 Baturić-Rubčić, J., 63
 Baudler, M., 130
 Bažant, V., 197
 Beagley, B., 110
 Beauchamp, J. L., 127
 Beavers, W. A., 195
 Beck, J. D., 115
 Beck, W., 151
 Becker, H. J., 108
 Bedos, R., 68
 Beg, M. A. A., 174
 Beier, B. F., 96
 Bellon, P. L., 205
 Benfield, F. W. J., 179
 Berau, G., 175
 Bergendahl, T. J., 177
 Berkowitz, J., 115
 Berne, B. J., 16, 34
 Bernstein, E. R., 150
 Bernstein, P. K., 178
 Berreman, D. W., 53
 Bertelo, C. A., 185
 Bezot, P., 18
 Bhatnagar, S. S., 67
 Bhattacharya, S., 56
 Bird, R. B., 5
 Birnbaum, G., 25
 Bitter, W., 112
 Bizot, K. F., 178
 Bjoerseth, A., 195
 Black, D. L., 111
 Black, J. D., 198
 Blackburn, J. F., 185
 Blake, M. R., 172
 Bland, W. J., 184
 Blinc, R., 40, 41, 58
 Blinn, E. L., 173
 Blinov, L. M., 60
 Bliot, F., 19
 Blount, J. F., 140
 Bock, C. R., 200
 Bock, E., 35
 Bock, M., 130
 Bock, P. L., 185
 Boden, N., 37
 Bodkin, C. L., 135
 Böhlend, H., 153
 Boehm, J. R., 178
 Boggess, R. K., 178
 Boilini, E., 33
 Bonfoey, D. B., 173
 Bopp, T. T., 29
 Borel, J., 33
 Boschetto, D. J., 185
 Bosnich, B., 173

- Bossu, F. P., 177
 Bottomley, F., 167
 Bottrill, M., 215, 216
 Boucher, L. J., 159, 160
 Bouligand, Y., 53, 54
 Bounthakna, T., 191
 Bowen, A. R., 154
 Boyd, J. R., 49
 Bracher, G., 210
 Brainina, E. M., 198
 Brandl, A., 156, 157
 Brateman, P. S., 198, 211
 Brauer, D. J., 206
 Brauman, J. I., 162
 Breitenbach, J., 68
 Brintzinger, H. H., 184
 Brochard, F., 53, 62
 Brocklehurst, B., 75, 77
 Brondeau, J., 21
 Brookes, G., 178
 Brot, C., 18, 27
 Brown, D. L. S., 192
 Brown, J. M., 217
 Brown, L. D., 96, 168
 Brown, M. P., 212
 Brown, T. L., 200, 203
 Browning, J., 218
 Brueser, W., 197
 Bruice, T. C., 165
 Brûlet, C. R., 156
 Brunvon, J., 195
 Bryan, P. S., 111
 Bryce, W. A., 68
 Brynor, J. B., 178
 Bryukhova, E. V., 152
 Bucaro, J. A., 25, 27
 Buchachenko, A. L., 67, 70
 Buchanan, D. H., 185
 Bûnder, W., 195
 Burce, G. L., 177
 Burger, M., 40
 Burk, P. L., 193
 Burlitch, J. M., 194
 Burness, J. H., 168
 Burnham, R. A., 192
 Burns, R. E., 111
 Busch, D. H., 173, 207
 Bush, R. D., 188
 Busolin, P., 43
 Butcher, R. J., 173
 Butler, S., 77
 Butler, W., 155, 196
 Byers, B. H., 200

 Calabrese, J. C., 170
 Calhoun, H. P., 132
 Callahan, K. P., 101, 105, 106
 Cameron, T. S., 132
 Candau, S., 47
 Candau, S. J., 24
 Cardin, D. J., 180, 193
 Cariati, F., 205
 Carnowa-Guzman, E., 183, 208

 Carr, D. D., 193
 Carreira, L. A., 129
 Carrigan, C. R., 60
 Carter, R. O., 110
 Carty, A. J., 174, 175, 204, 214
 Casey, C. P., 197
 Casey, F. A., 180
 Cassar, L., 174
 Cassoux, P., 111
 Cava, M. P., 141
 Cegielsky, R., 67
 Cenini, S., 176
 Ceriotti, A., 205
 Cernia, E., 116
 Cesari, M., 116
 Cetinkaya, B., 180, 181
 Chamberlain, J., 21
 Chan, S., 101
 Chandrasekhar, S., 63
 Chang, C. K., 162, 164
 Chang, J. J., 37
 Chang, R., 33
 Charrolin, J., 37
 Chatt, J., 156, 157, 174
 Chellappa, K. L., 177
 Cheney, R., 173
 Cheng, P. T., 217
 Cherwinski, W. J., 175
 Cheung, P. S. Y., 14
 Chieh, P. C., 174, 214
 Chigrinov, V. G., 60
 Chini, P., 203, 205
 Chisholm, M. H., 152, 155, 210
 Christe, K. O., 127, 145
 Christensen, J. J., 140
 Christensen, S., 56
 Chu, K. S., 42
 Chung, C., 180
 Churchill, M. R., 176
 Chvalovsky, V., 197
 Ciani, G., 205
 Cihonskii, J. L., 137
 Cinquini, M., 138
 Cladis, P. E., 55, 63
 Clark, C. R., 169
 Clark, H. C., 174, 210
 Clark, N. A., 34
 Clark, R. J. H., 154
 Clarke, M. J., 166
 Clarke, R. E., 167
 Clarkson, S. C., 167
 Clendening, P. J., 177
 Clugston, M. J., 70
 Coates, G. E., 95
 Coe, C. G., 160
 Cohen, M. A., 203
 Collier, M. R., 180
 Collins, D. M., 155
 Collins, S., 68
 Collman, J. P., 162, 164
 Colton, R., 194, 204
 Commons, C. J., 194, 204
 Conlin, R. T., 120
 Conneely, J. A., 217

 Connor, J. A., 192
 Constant, E., 19
 Conti, F., 176
 Conway, A. J., 116, 194
 Cooper, M. J., 96
 Cooper, N. J., 180
 Corben, J. L., 159
 Corbett, J. D., 123
 Corbridge, D. E., 92
 Corey, J. Y., 188
 Corigliani, F., 153, 154
 Corrigan, M. F., 170
 Corriu, R. J. P., 191
 Coskran, K. J., 173
 Cotter, M. A., 33
 Cotton, F. A., 154, 155, 161, 183, 186, 194, 201, 202, 204
 Cotton, S. A., 92
 Craddock, S., 120
 Cragg, R. H., 112
 Cram, D. J., 138
 Crane, G. R., 153
 Creaser, C. S., 149
 Creaser, I. I., 171
 Creighton, J. A., 149
 Cresswell, R. A., 111
 Cripps, H. N., 88
 Crociani, B., 152
 Cross, R. J., 211
 Croxton, C. A., 6
 Cruickshank, D. W. J., 132
 Crumbliss, A. L., 180
 Cucinella, S., 116
 Cummack, R., 166
 Cummins, P. G., 43
 Curtis, M. D., 155, 196
 Curtis, N. F., 173
 Curtis, W. D., 137
 Curtiss, C. F., 5
 Cusachs, L. C., 115
 Cutler, R. S., 195
 Czira, G., 192

 Dabrowiak, J. C., 173
 Dahl, A. R., 120
 Dahl, L. F., 205
 Dahler, J. P., 70
 Dahlmann, W., 123
 Dalley, N. K., 140
 Daly, J. J., 123
 Dance, I. G., 170
 Daneshrad, A., 190
 Dang, T. P., 171
 Daniels, W. B., 63
 Dapporto, P., 172, 208
 Dardy, H., 24
 Darnon, I., 27
 Dasannacharya, B. A., 16
 Davidson, I. M. T., 119
 Davidson, J. L., 186, 216
 Davidson, P. J., 182
 Davies, G. J., 21
 Davies, M., 17, 19, 21, 44
 Davis, A. R., 150

- Davis, R., 216
 Davison, A., 150
 Day, P., 125
 Day, V. W., 150, 157, 160
 DeBoer, B. G., 176
 de Boer, J. L., 184
 Debrunner, P. G., 163
 Degenkolb, E. O., 77
 de Gennes, P. G., 31, 65
 Dehmer, J. L., 115
 Delhez, R., 67
 De Liefde-Meijer, H. J., 184
 Deloche, B., 37
 Del Piero, G., 116
 Delpuech, J. J., 115
 Demers, J. P., 185
 DeStefano, A., 112
 Deuling, H. J., 53
 Deutch, J. M., 16
 Deutsch, E., 170
 Devaure, J., 25
 Dewan, J. C., 150
 de Zwart, M., 60
 Diaddario, L. L., 178
 Diamantis, A. A., 157, 166
 Dianoux, A. J., 46
 Dickinson, R. J., 172
 Diehl, P., 35
 Di Gennaro, T. M., 29
 Dill, J. F., 25
 Dillard, J. G., 168
 Dillon, K. B., 174
 Dilworth, J. R., 156
 Di Pasquale, S., 153, 154
 Dixon, D. A., 96
 Dixon, K. R., 175
 Dixon, R. S., 75
 Doane, J. W., 41, 58
 Dobbs, A. J., 72, 81
 Doedens, R. J., 177
 Dötz, K. H., 181
 Dolphin, D., 164, 174
 Domiano, P., 173
 Domka, F., 67
 Donaldson, J. D., 125
 Dong, R. Y., 35
 Doonan, D. J., 175, 206
 Dori, Z., 168
 Dormond, A., 150, 191
 Dougherty, J. P., 118
 Doyle, M. J., 180, 193
 Dozzi, G., 116
 Drake, J. E., 120
 Dreher, R., 53
 Drew, M. G. B., 149
 Druskovich, D. M., 154
 Dubois, J. E., 193
 Dubois-Violette, E., 60
 Ducruix, A., 206
 Duggan, D. M., 177
 Dullenkopf, W., 123
 Dunmur, D. A., 43
 Dunn, J. G., 184
 Durand, G., 32, 60
 Durig, J. R., 110, 111, 129
 Dustin, D. F., 101
 Dvolaitzky, M., 37
 D'yakov, V. M., 190
 Dyarek, D., 63
 Dye, J. L., 123
 Dyson, J., 132
 Dzyaloshinskii, I. E., 53
 Eaborn, C., 190
 Eady, C. R., 179
 Ebner, J. R., 161
 Ebsworth, E. A. V., 120
 Eckberg, R. P., 177
 Edwards, D., 184
 Edwards, P. A., 123
 Efner, H. F., 179
 Egelstaff, P. A., 9, 16
 Eidenschen, R., 190
 Einstein, F. B., 150
 Eisch, J. J., 108, 116, 187
 Eisenberg, R., 175, 206
 Eley, D. D., 69
 Elian, M., 199
 Ellis, J. E., 196
 Ellis, P. D., 110
 Elmitt, K., 184
 Elson, I. H., 211
 Ely, N., 183
 Elzaro, R. A., 111
 Empsall, H. D., 100, 171
 Emsley, J. W., 35, 37
 Endell, R., 156, 157
 Enemark, J. H., 178
 Engelhardt, G., 190
 Engler, E. M., 141
 Epstein, I. R., 96
 Erbland, M. L., 129
 Esparza, F., 130
 Etemad, S., 141
 Evans, G. J., 19
 Evans, G. T., 70, 80
 Evans, I. P., 167
 Evans, J., 201, 203
 Evans, M., 19, 21, 26, 39, 44
 Evans, R. H., 140
 Evans, W. J., 101, 106
 Everett, G. W., 167
 Ewings, P. F. R., 124
 Extine, M., 152, 155
 Fabelinskii, I. L., 21
 Faber, T. E., 53, 58
 Fachinetti, G., 185, 196
 Faller, J. W., 183
 Fallon, G. D., 170
 Faltynek, R. A., 196
 Farkas, L., 69
 Farrar, T. C., 29
 Farrugia, L., 197
 Faulkner, L. R., 83, 84, 85
 Fawcett, J. P., 200
 Fay, R. C., 150, 152
 Felkin, H., 206
 Fellner, H., 56
 Felter, K., 97
 Felton, R. H., 174
 Feltz, A., 153
 Ferguson, G., 170, 173
 Fick, H. G., 151
 Figueras Roca, F., 67
 Fild, M., 129
 Finn, P. A., 152
 Finocchiaro, P., 152
 Fischer, E. O., 181
 Fischer, R. G., 204
 Fisher, R. C., 159
 Fitzpatrick, N. J., 110
 Flinders, P. J., 50
 Floriani, C., 185, 196
 Foa, M., 174
 Foley, P., 124
 Fong, C. W., 212
 Foord, A., 110
 Ford, P. C., 167, 171
 Forder, R. A., 184
 Forster, A., 203
 Forster, D., 16, 55
 Franczek, F. R., 168
 Frank, A., 130, 181
 Frank, U., 123
 Franke, R., 190
 Frankel, R. B., 164, 165
 Frankevitch, E. L., 78
 Franklin, W., 42, 56
 Franks, M. L., 154
 Franulović, K., 63
 Fredrickson, A. G., 40
 Freed, J. H., 45, 75
 Frenz, B. A., 154, 155, 161
 Frlec, B., 146
 Füller, H. J., 190
 Fujita, I., 174
 Fumagelli, A., 203
 Furman, R., 167
 Gabay, M., 53
 Gagne, R. R., 162
 Gainsford, G. J., 194
 Galerne, Y., 44, 60
 Galle, J. E., 108
 Gallici, R. R., 187
 Galyer, L., 209
 Garber, A. R., 97
 Gardy, E. M., 75
 Gargano, M., 207
 Garito, A. F., 141, 142
 Garner, C. D., 152, 155, 158
 Garnett, J. L., 172
 Garnier, F., 193
 Gartzke, W., 156
 Gaspar, P. P., 120
 Gass, D. M., 16
 Gasser, O., 190
 Gatehouse, B. M., 170
 Gaughan, A. P., jun., 118
 Gay, R. S., 150
 Gearhart, R. C., jun., 115

- Gebala, A. E., 183
 Gebbie, H. A., 21
 Gebert, E., 145
 Geiger, W. E., 175
 Geoffroy, G. L., 169
 George, T. A., 157
 Gerritsma, C. J., 54
 Gerschel, A., 27
 Getz, D., 168
 Ghosh, S. K., 33
 Giannoccaro, P., 207
 Gibbins, S. G., 151
 Gibson, J. F., 209
 Giguère, P. A., 127
 Gill, J. T., 99
 Gillard, R. D., 217
 Ginley, D. S., 155, 196, 199
 Gloviovov, I. P., 188
 Goddard, R., 215, 216
 Goggin, P. L., 175
 Gokel, G. W., 138
 Goldberg, S. Z., 175, 206
 Goldwhite, H., 129, 130
 Golino, C. M., 188
 Gong, H., 101
 Gonzalez, B., 159
 Good, R., 151
 Goodall, B. L., 168
 Goodfellow, R. J., 175
 Gordon, R. G., 19
 Goren, S. D., 58
 Gornall, W. S., 25
 Goscianski, M., 60
 Goto, M., 153
 Goubeau, J., 123
 Goulon, J., 21
 Govil, S., 153
 Gowenlock, B. G., 195
 Graf, E., 139
 Graves, V., 179
 Gray, G. W., 31
 Gray, H. B., 168, 169, 170, 177, 178
 Grebenkin, M. F., 60
 Green, D. K., 29
 Green, M., 106, 186, 214, 215, 216, 218
 Green, M. L. H., 179, 180, 184, 194, 197
 Greenwood, N. N., 99
 Greffe, J.-L., 21
 Gregor, I. K., 172
 Greiss, G., 108
 Griend, L. J. V., 127
 Griffith, W. P., 149
 Grimes, R. N., 101, 106
 Groff, R. P., 80, 88
 Grubbs, R. H., 193
 Grunthaner, F. J., 177
 Gsell, R., 124
 Gubanova, L. I., 190
 Guengerich, G. P., 167
 Guerst, J. A., 54
 Guest, M. F., 152
 Guggenberger, L. J., 180, 196
 Gunsalus, I. C., 163
 Gupta, A., 74
 Gusel'nikov, L. E., 188
 Gust, D., 188
 Guyon, E., 49, 53, 55, 60
 Gysling, H., 183
 Haaland, A., 195
 Haas, C. H., 119
 Habeeb, J. J., 117
 Hackett, P., 196
 Haddock, S. R., 175
 Hadjiminolis, S., 125
 Haffmanns, R., 19
 Hagen, K., 126
 Haines, R. J., 193
 Hakemi, H., 40, 41
 Halbert, T. R., 162
 Halgren, T. A., 96
 Hall, J. H., jun., 96
 Hall, L. W., 110
 Halperin, B. I., 65
 Halpern, J., 168, 210
 Halstead, G. W., 183
 Halstenberg, M., 132
 Hammond, G. S., 74, 169, 195
 Hanes, R. M., 218
 Hannan, W., 172
 Harke, E., 153
 Harp, G. D., 16
 Harris, D. C., 201
 Harris, D. H., 124
 Harris, R. K., 129
 Harris, R. O., 156
 Harrison, P. G., 124
 Harrod, J. F., 152
 Hart, D. W., 185
 Hart, F. A., 92
 Hartman, J. S., 111
 Hartshorn, A. J., 181
 Hasegawa, M., 88
 Hatfield, W. E., 177
 Hatzenbuehler, D. A., 180
 Haupt, H. J., 116
 Haworth, D. T., 112
 Hawthorne, M. F., 96, 99, 101, 105, 106, 108
 Hayashi, H., 88
 Hayes, C. F., 56
 Heath, G. A., 157, 186
 Heaton, B. T., 203
 Hedberg, K., 126
 Hedberg, L., 126
 Heeger, A. J., 142
 Heger, J. P., 34
 Heidemann, A., 42
 Heil, C. A., 120
 Heil, H. F., 108
 Heimrod, G. W., 67
 Helm, F. T., 177
 Hendrickson, A.-R., 170, 177
 Hendrickson, D. N., 177
 Hennig, H. J., 120
 Herberich, G. E., 108
 Herstein, F. H., 143
 Herman, Z. S., 142
 Hermanek, S., 97
 Hermann, T., 140
 Herschaft, A., 123
 Herskovitz, T., 164, 165, 166
 Hervet, H., 46
 Hetflejs, J., 197
 Hewitt, R. C., 40, 50
 Hexmeier, R. J., 155
 Heyman, L. E., 173
 Hidai, M., 159
 Higashimura, T., 77
 Hildebrandt, R. L., 97
 Hill, J. D., 96
 Hill, N. E., 17
 Hill, W. E., 105
 Hillier, I. H., 152
 Hirayama, Y., 178
 Hirschfelder, J. O., 5
 Hitchcock, P. B., 116, 181, 194
 Ho, J. T., 63
 Hoa, K., 172
 Hobdell, M. R., 94
 Hodges, H. L., 129
 Hodges, K. C., 214
 Hodges, R. J., 176
 Hodges, R. V., 127
 Hodgson, K. O., 183
 Hoeg, D. F., 180
 Hoel, E. L., 96, 105
 Hoffman, K., 187
 Hoffman, M. Z., 167
 Hoffmann, B. M., 159, 160, 162, 164, 167
 Hoffmann, R., 199
 Hohorst, F. A., 145
 Holloway, J. H., 146, 147
 Holm, R. H., 164, 165, 166, 170, 174
 Holmerda, R. A., 178
 Holzinger, W., 182
 Hoof, D. L., 151
 Hoover, W. G., 14
 Hoskins, A. F., 194
 Hoskins, B. J., 204
 Hosmane, N., 120
 Hosokawa, T., 174
 Hota, H. K., 108
 Howard, A. V., 119
 Howard, J. A., 214
 Howard, W. F., 143, 144, 145
 Howard-Lock, H. E., 25
 Howe, R. F., 168
 Howells, W. S., 42
 Hoytink, G. J., 84
 Hrcir, D. C., 184
 Hsieh, A. T. T., 116, 194, 198
 Huang, C. C., 63
 Huang, J.-T. J., 77
 Hubbard, P. S., 25
 Huber, H., 198, 199
 Hubert-Pfalzgraf, L. G., 153

- Hudson, A., 198
Huff, L., 129
Huffmann, J. C., 97
Hughes, R. E., 194
Hughes, R. P., 215, 216
Hughey, J. L., 200
Huheey, J. E., 92
Hui, E., 151
Hull, J. R., 179
Hunter, D. L., 201, 202
Huttner, G., 130, 181
Hyde, E. M., 171
Hyde, M. R., 158
- Iannuzzi, M. M., 154
Ibers, J. A., 162, 163, 164, 165, 167, 170, 176
Ichikawa, M., 158
Iitaka, Y., 170
Inglis, T., 154, 213
Ioganson, A. A., 198
Isbe, S. D. A., 157
Ishaq, M., 180
Ishigino, M., 187
Ishii, Y., 170
Ishikawa, M., 187
Ishizu, K., 178
Isred, S. S., 166
Ito, T., 196
Itoh, K., 170
Ittel, S. D., 176
Ivanov, D., 197
Ivanov, L. L., 195
Izatt, R. M., 140
- Jablonski, C. R., 210
Jack, T. R., 217
Jackson, R. A., 200
Jackson, W. G., 173, 203
Jacobson, S. E., 175
Jaecker, J. A., 161
Jähnig, F., 62
Jaenicke, O., 179
Janik, J. A., 47
Janik, J. M., 47
Jaouen, G., 191
Jarkowitz, D., 150
Jarvis, J. A. J., 217
Jaworiwsky, I. S., 98
Jefferson, I., 184
Jeffery, J. W., 114
Jellinek, F., 184
Jen, S., 34
Jenks, J. M., 142
Jennische, P., 118
Jensen, F. R., 185
Job, R. G., 165
Joblin, K. N., 198
Johns, W. S., 210
Johnson, A. W., 198
Johnson, B. F. G., 175, 201, 203
Johnson, D. L., 39
Johnson, F. A., 105
Johnson, H. D., jun., 98
Johnson, M. H., 75
Johnson, R. C., 78
Johnson, W. B., 152
Joklik, J., 197
Jolly, W. L., 151
Jonas, K., 194
Jones, C. J., 101
Jones, G. H., 137
Jones, J., 29
Jones, J. T., 75
Jones, M., 187
Jones, T. E., 178
Joy, G., 118
- Kabre, T. S., 118
Kadooka, M. M., 178
Kagan, H. B., 171
Kalasinsky, V. F., 111
Kalbfus, W., 181
Kamha, M. A., 70
Kaminsky, W., 196
Kaneke, S., 68
Kapon, M., 143
Kapoor, P. N., 153
Kaptein, R., 70
Kapur, R. N., 67
Karakida, T., 153
Karsch, H. H., 212
Kasai, P. H., 180
Katoric, V., 155
Katz, J. J., 193
Keeton, M., 217
Keiderling, T. A., 150
Kelling, H., 190
Kellogg, R. E., 80
Kembler, M., 176
Kemmitt, R. D. W., 184
Kendurkar, P. S., 190
Kennelly, W. J., 100
Kepert, D. L., 150, 154
Kesthelyi, C. P., 85
Kettersen, J. B., 56
Keulen, E., 123
Keyes, P. H., 63
Keyes, T., 25
Khaddar, M. R., 115
Khan, M. T., 172
Khane, G. P., 168
Khotsianova, T. L., 152
Kidd, D. R., 203
Kiefer, G. W., 158
Kielich, S., 17
Kiener, V., 181
Kiernan, P. M., 149
Kiffen, A. A., 175, 176
Kilgour, J. A., 187, 188
Kilner, M., 154, 213
Kilty, P. A., 152
Kimura, E., 170
King, M. S., 152
King, R. B., 153, 214
- Kingston, B. M., 180
Kirner, J. K., 159
Kivelson, D., 25
Klabunde, K. J., 179
Kleier, D. A., 96
Klein, H. F., 212
Kleine, W., 181
Kléman, M., 63, 64
Klemperer, W., 77
Klinger, R. J., 155, 196
Knobler, C. B., 105
Knol, J., 184
Knowles, W. S., 171
Ko, D., 130
Kobayashi, A., 208
Koch, S., 164
Kochi, J. K., 211
Kodama, H., 153
Koerner von Gustorf, E. A., 179
Kohler, F. H., 190
Kolari, H. J., 154
Kolb, J. R., 100, 151, 183, 196
Kolobova, N. E., 198
Kolosov, E. E., 68
Korn, C., 58
Kouba, J., 159
Kovar, R. A., 112
Kozima, S., 108
Kramer, A. V., 211
Kramer, P. A., 176
Krause, A., 67
Krausz, P., 193
Krebs, P., 32, 39
Kreis, G., 181
Kreissl, F. R., 181
Kreiter, C. G., 181
Krishnamurthy, S. S., 132
Krishnamurti, D., 33
Krogsrund, S., 176
Kroneck, P., 178
Kroto, H. W., 111
Kruchna, O., 197
Kruczynski, L., 201
Krüger, C., 206
Krüger, G. J., 41
Kruglaya, O. A., 183
Kubarev, S. I., 75
Kubo, R., 9
Kubota, M., 171
Kuchitsu, K., 153
Kuczkowski, R. L., 111
Kuczynski, W., 33
Kündig, E. P., 198, 199
Kugel, R. L., 132
Kuhn, N., 132
Kumada, M., 187
Kuremire, E. M. R., 167
Kuroda, R., 118
Kurras, E., 190
Kushick, J., 34
Kuznesof, P. M., 111
Kuznetsov, S. L., 152
Kyper, J., 178

- Labarre, J. F., 112
 Labert, R. L., 187
 Labes, M. M., 40, 41
 Labhart, H., 86
 Labinger, J. A., 185, 196
 Lachowitz, A., 196
 LaCour, T., 186
 Lagerwall, S. T., 60
 Lagow, R. J., 180
 Lagowski, J. J., 179
 Laguna, A., 214, 218
 Lahuerta, P., 201
 Laidler, D. A., 43, 137
 Laing, M., 169
 Lakshmikanthan, M. V., 141
 Lambert, T. P., 77
 Lang, G., 162
 Langbein, H., 153
 Lappert, M. F., 108, 111, 115,
 124, 127, 151, 180, 181,
 182, 192, 193
 Larcher, F., 191
 Larkin, I., 44
 Larkin, I. W., 19
 Larson, S. B., 140
 Lascombe, J., 25
 Laskowski, E. J., 177
 Lathouwers, Th. W., 60
 Laurie, S. H., 178
 Lawler, R., 70
 Leadbetter, A. J., 42
 Leblanc, J. C., 150, 191
 Le Blanc, M., 195
 Lechert, H., 120
 Lechner, R. E., 46
 Leclerc, B., 118
 Lednor, P. W., 198
 Ledwith, D. A., 158
 Léger, L., 53, 60
 Legg, J. I., 169
 Lehmann, T. V., 108
 Lehn, J. M., 139
 Leigh, G. J., 157, 193
 Lemley, J. T., 142
 Le Moigne, F., 150, 191
 Leshina, T. V., 70
 Lesin, B. I., 78
 Letsou, A., 130
 Leung, M. L., 192
 Levason, W., 172
 Levenson, R. A., 137
 Levesque, D., 14, 15
 Levine, Y. K., 37
 Levy, D. H., 77
 Lewis, B., 216
 Lewis, D. F., 150
 Lewis, D. L., 196
 Lewis, J., 175, 201, 203
 Leyden, R. N., 99, 108
 Liebert, L., 37
 Lightowlers, D., 37
 Lin, H. S., 168
 Lin, W. J., 63
 Lindmark, A. F., 152
 Lindon, J. C., 35, 37
 Lindsell, W. E., 195
 Lindstrom, R. H., 132
 Lippard, S. J., 99, 150, 196
 Lipscomb, W. N., 96
 Litovitz, T. A., 24, 25, 27
 Litster, J. D., 32
 Little, R. G., 163
 Litzow, M. R., 111
 Liu, C., 140
 Lloyd, M. K., 215, 216
 Lo, F. Y., 106
 Lo, S. T. D., 173
 Loayza, N., 141
 Lockhart, S. H., 120
 Loescher, B. R., 156
 Lohr, L. L., 184
 Long, M. A., 172
 Longini, G., 205
 Longuet-Higgins, H. C., 9
 Lopata, V. J., 75
 Lorenz, H., 130, 181
 Lottes, K., 151
 Lovesey, S. W., 9
 Lower, L. D., 205
 Lowie, C. M., 170
 Lowry, B. A., 49, 56
 Lubensky, T. C., 63, 65
 Luckhurst, G. R., 34, 35, 37,
 39, 44
 Lukosius, E. J., 173
 Lund, T., 178
 Lunsford, J. H., 168, 171
 Lusk, D. I., 180
 Luszyk, J., 195
 Luz, Z., 40
 Luzar, M., 40, 41
 Mabbott, D. J., 218
 Mabbbs, F. E., 158
 McCaffrey, D. J. A., 203
 McCauley, R. E., 152, 155
 McCauliffe, C. A., 172
 McClung, R. E. D., 19
 McColl, J. R., 34, 39
 MacDiarmid, A. G., 142
 McDonald, J. W., 159
 McFarlane, H. C. E., 129
 McFarlane, W., 129
 McGee, H. A., jun., 112
 McGinnis, J., 193
 McGlinchey, M. J., 120, 179
 Machin, D. J., 177
 McIntyre, D., 13
 McKee, T. J., 39
 MacKenzie, R., 214
 McLauchlan, K. A., 72, 81
 McLaughlin, G. M., 180
 McLendon, G., 169
 McLeod, D., 180
 McLeod, T., 175
 McLick, J., 188
 McMillan, W. L., 40, 62
 McNelis, E., 193
 McQueen, D. H., 56
 McQuillin, F. J., 92
 McTague, J. P., 25
 McVicker, E. M., 129
 McVicker, G. B., 194
 Madan, V., 185
 Maeda, K., 174
 Magee, J. L., 77
 Magelee, L. A., 188
 Maier, M., 111
 Maitlis, P. M., 208, 218
 Malet, G., 54
 Malmberg, M. S., 29
 Mal'tsev, A., 192
 Manassero, M., 205
 Mango, F. D., 193
 Maniantov, G., 145
 Mannan, K., 132
 Manne, R., 115
 Manning, A. R., 196
 Manojlovic-Muir, Lj., 175
 Mantovani, A., 210
 Maranelli, R. S., 160
 Marčelja, S., 36
 March, F. C., 157, 171
 Marcieniec, B., 67
 Marek, H., 68
 Mares, F., 183
 Margerum, D. W., 177
 Marignan, J., 54
 Markarian, Sh. A., 70
 Marks, S. B., 58
 Marks, T. J., 100, 151, 183, 196
 Marquardt, G., 188
 Marryot, A. A., 29
 Marsh, R. E., 168
 Marshall, W., 9
 Marsili, M., 130
 Marstokk, K. M., 195
 Martell, A. E., 169, 172
 Martin, J. L., 149
 Martin, R. B., 178
 Martin, R. L., 170, 177
 Martinengo, S., 203, 205
 Martinoty, P., 47
 Martire, D. E., 33
 Maslen, H. S., 160, 178
 Mason, R., 157, 171, 174, 186,
 217
 Masood-ul-Hasan, 132
 Masters, C., 175, 176
 Masuda, I., 160
 Matheson, K. L., 140
 Matheson, T. W., 201, 203
 Mathew, M., 175
 Mathews, N. J., 110
 Mathur, K. N., 67
 Matsuda, I., 170
 Matsuzaki, A., 78
 Matteson, D. S., 188, 197
 Matshita, T., 160
 Maugh, T. H., 162
 May, C. J., 217
 Mayerle, J. J., 165

- Mays, M. J., 194
Maze, C., 39
Mazzei, A., 116
Mealli, C., 172
Meek, D. W., 174
Mehrotra, R. C., 153
Mehrotra, S. K., 153
Meiboom, S., 40, 50
Mein, F., 194
Melamud, E., 168
Melson, G. A., 173
Meneghelli, B. J., 101
Menig, H., 186
Mennenger, H., 190
Mente, D. C., 111, 127
Mentzer, E., 100
Merbach, E., 151
Mercer, G. D., 101
Merdak, S. J., 176
Merrell, P. H., 173
Merrifield, R. E., 67, 78, 80
Merryman, D. J., 123
Mertis, K., 183, 208, 209
Meshitsuka, S., 158
Meyer, A., 191
Meyer, R. B., 53
Meyer, R. J., 40
Meyer, T. J., 200
Michalik, M., 190
Michalski, J., 135
Middleton, R., 179
Midollini, S., 172, 208
Mikotajczak, J., 135
Mikulski, C. M., 142
Millar, M., 174
Miller, E., 67
Miller, J. R., 201
Miller, J. S., 175, 206
Miller, V. R., 101
Millington, D., 175
Mills, J. L., 111, 123, 127, 198
Milone, L., 203
Mircea-Roussel, A., 43, 44
Mishima, T., 88
Mishra, S. P., 127
Miskowski, V. M., 168
Mislow, K., 188
Mitsui, Y., 170
Miyano, K., 56
Mocella, M. T., 173, 174
Modinos, A., 175, 206
Möhwald, H., 39
Moelendal, H., 195
Mohai, B., 197
Moise, C., 150, 191
Mol, J. C., 193
Molia, Yu. N., 70
Mollere, P. D., 187
Mondal, P., 114
Moneland, J. A., 177
Montanari, F., 138
Monteil, Y., 123
Moody, D. C., 97
Moore, G. Y., 132
Moore, R. D., 184
Moorehead, E. L., 158
Morazzoni, F., 171
Moreau, J. J. E., 191
Mori, H., 9
Moritani, I., 174
Moriyama, H., 208
Moroi, D. S., 42
Morrell, D. G., 211
Morrison, J. A., 180
Morse, J. G., 174
Morse, K. W., 174
Mortensen, L. E., 165, 166
Moskovits, M., 199
Moss, K. L., 175
Moss, T. H., 166
Moulijn, J. A., 193
Moutron, R., 39
Müller, H.-D., 130
Müller, J., 181, 182, 186
Müller, W., 123
Münster, A., 10
Muetterties, E. L., 96
Muhr, G., 68
Muir, K. W., 159, 175
Mulay, I. L., 68
Mulay, L. N., 68
Munroe, S. E., 56
Murakashi, S. I., 174
Murray, K. S., 170
Murray, M., 214
Murray, S. G., 172
Murrell, J. N., 75
Murtha, D. P., 161
Murthy, A. R. V., 132
Musatti, A., 173
Musco, A., 183
Muscari, I., 56
Muttner, G., 156
Myers, E., 108
Nabi, S. N., 132
Nagai, S., 47
Nagakura, S., 78, 88
Naghizadeh, J., 15
Naik, D. V., 204
Nainan, K. C., 153
Nakajima, M., 208
Nakayama, H., 118
Naldini, L., 205
Nametkin, N. S., 188
Napoletano, T., 171
Nardelli, N., 173
Nardi, N., 172
Nefedov, O. M., 192
Nehring, J., 65
Neumann, F., 116
Newkome, G. R., 129
Newton, W. E., 159
Nicholson, B. K., 198
Nickerson, M. A., 58
Nicolini, M., 152
Niecke, E., 112
Nielsen, S. E., 70
Nien, T., 174
Nishikida, K., 145
Nisselson, L. A., 152
Noack, F., 58
Nolte, M. J., 169
Nordio, P. L., 35, 43
Norman, A. D., 120
Norman, J. G., 154
Norman, T. R., 166
Norton, J. R., 175
Novak, R. W., 105
Nyburg, S. C., 217
Oakley, R. T., 132
Ochs, J., 190
Odom, J. D., 110, 111, 129
Oehme, G., 190
Ogata, I., 171
Ogden, J. S., 179
Ohi, F., 187
Oliver, A. J., 208
Oliver, J. P., 194
On, P., 188
Onak, T., 92
O'Neal, H. E., 119
O'Neill, P. S., 196
Opitz, R., 197
Oppenheim, E., 39
Orbell, J. D., 169
Orioli, P. L., 172
Ornstein, L. S., 10
Osborn, J. A., 211
Osthurd, N. S., 144
Otnes, K., 47
Overzet, F., 184
Ozin, G. A., 198, 199
Paddock, N. L., 132
Paik, H. N., 214
Palenik, G. J., 175, 204
Pamphilis, B. V., 165
Panaiotiev, I., 197
Paningo, E. B., 177
Pardoe, G. W. F., 21
Parish, R. V., 172
Parker, C. A., 83
Parker, G., 206
Parodi, O., 54
Parry, G., 93, 94, 95
Parsons, J. D., 56, 60
Pascard, C., 206
Pasinskii, A. A., 198
Pasteur, G. A., 153
Patel, H. A., 204
Patel, V. V., 141
Patil, D. S., 192
Pattison, P., 96
Paul, I. C., 173
Paz-Andrade, I. M., 192
Pearce, R., 182
Pearman, A. J., 156
Pedersen, C. T., 141
Pedersen, E., 154, 161

- Pedersen, S. G., 116
 Pederson, S. W., 194
 Pedley, J. B., 111, 115, 127, 151, 192
 Peguy, A. A., 115
 Pell, S. D., 167
 Penka, V., 69
 Penney, G. J., 123
 Penney, T., 141
 Penz, P. A., 60
 Perego, G., 116
 Perisamy, N., 83, 87
 Perrin, D. D., 178
 Perrot, M., 25
 Pershan, P. S., 34, 64
 Pessine, F. B. T., 111
 Pettit, L. D., 178
 Philips, D. A., 171
 Phillips, W. D., 165
 Piciulo, P. L., 161
 Pierce-Butler, M., 126
 Piersanski, P., 49, 53, 55, 60
 Pikin, S. A., 60
 Pilbrow, M. F., 217
 Pindak, R. S., 63
 Pines, A., 37
 Pink, D. A., 36
 Pinnavaia, T. J., 149
 Pinnow, D. A., 24
 Pirš, J., 40, 41
 Pittman, C. U., jun., 218
 Pitzer, K. S., 148
 Plešek, J., 97
 Plummer, J. F., 152, 174
 Pluth, J. J., 168
 Podolsky, G., 149
 Poë, A. J., 198, 200
 Poggi, Y., 33
 Poldy, F., 37
 Polichnowski, S. W., 197
 Polnaszek, C. F., 45
 Pompeiro, A. J. L., 159
 Pong, R. G. S., 115
 Poolton, D. S. P., 152
 Pople, J. A., 96
 Popowski, E., 190
 Porter, R. F., 112
 Poskozim, P. S., 170
 Poulin, J. C., 171
 Poupkov, R., 34, 39
 Powell, J., 217
 Powles, J. G., 13, 14, 28, 29
 Prabha, C. S., 33
 Pregosin, P. S., 210
 Preut, H., 116
 Price, A. G., 17
 Price, A. H., 39, 43
 Priestley, E. B., 32, 34
 Pritzkow, H., 118
 Prost, J., 64
 Prout, C., 194
 Prout, K., 184
 Pshenichnov, E. A., 75
 Puddephatt, R. J., 212
 Pulham, R. J., 93, 94, 95
 Pusatcioglu, S., 112
 Pye, P. L., 181
 Que, L., 165
 Quentrec, B., 14, 18
 Quinn, M. J., 75
 Rahman, A., 14
 Rakowski, M. C., 207
 Ranchfuss, B., 174
 Randall, E. W., 203
 Ranganathan, J. N., 132
 Rao, K. R., 16
 Rapini, A., 56
 Rasmussen, J. R., 185
 Raston, C. L., 150
 Rathousky, J., 197
 Rault, J., 54
 Rausch, M. D., 184
 Raymond, K. N., 168, 183
 Raymond, L., 176
 Reade, W., 110
 Reed, C. A., 159, 162
 Reeves, W. B., 68
 Rega, H. U., 39
 Reichert, W., 155
 Reinsch, E. A., 70
 Remmel, R. J., 98
 Restivo, R. J., 173
 Reynolds, R., 39
 Rhee, S. G., 116
 Rhine, W. E., 194
 Rice, S. A., 15
 Richards, R. L., 152, 156, 159
 Richter, F., 68
 Riddle, C., 120
 Riedel, E. F., 145
 Rieger, P. H., 154
 Riess, J. G., 153, 195
 Rietz, R. R., 151
 Rigatti, G., 43
 Rigny, P., 28
 Riley, P. N. K., 111
 Ring, M. A., 119
 Rivail, J. L., 21
 Robbins, J. L., 168
 Robert, J., 33
 Roberts, J. D., 201
 Roberts, P. J., 170
 Robinson, B. H., 203
 Robinson, P. R., 158
 Robinson, S. D., 170
 Robinson, W. R., 116, 161
 Robinson, W. T., 106, 162
 Rodesiler, P. F., 195
 Rondelez, F., 40, 43, 44, 60
 Root, C. A., 170
 Rorabacker, D. B., 178
 Rościszewski, K., 42, 46, 47
 Rosenberg, E., 201, 203
 Rosenberg, R. C., 170, 178
 Rosenthal, I., 67
 Rosenthal, U., 190
 Ross, S. D., 125
 Rossi, M., 207
 Rost, C. A., 178
 Rothgery, E. F., 112
 Rothschild, A. J., 187
 Roundhill, D. M., 174
 Routledge, V. I., 158
 Rowley, R. J., 212
 Rowlinson, J. S., 6
 Royle, G., 191
 Royston, G. M. D., 159
 Ruben, D. J., 37
 Rubini, P. R., 115
 Rudolph, R. W., 101
 Rumyantsev, B. M., 78
 Rupprecht, G., 161
 Rushbrooke, G. S., 6, 10
 Rusin, B. M., 78
 Russek, A., 197
 Russell, D. R., 217
 Russo, P. J., 142
 Rutar, V., 58
 Sabachy, M. J., 171
 Sacco, A., 207
 Sacconi, L., 172, 173, 208
 Sachsse, H., 69
 Sackmann, E., 32, 39
 Sagdeev, R., 70
 Sahajpal, A., 170
 St. Pierre, A. G., 25
 Saito, T., 208
 Saito, Y., 118
 Sakuragi, H., 88
 Sakuragi, M., 88
 Salentine, C. G., 96, 101, 105
 Salikhov, K. M., 70
 Sanders, J. R., 176
 Sansoni, M., 205
 Santhanam, K. S. V., 83, 87
 Santini, G., 195
 Saran, M. S., 142
 Sargent, F. P., 75
 Sargeson, A. M., 167, 171
 Sasaki, Y., 208
 Sato, S., 118
 Sau, A. C., 132
 Sauer, J. D., 129
 Saupe, A., 65
 Savoie, R., 127
 Schaaf, T. F., 151
 Schack, C. J., 127
 Schaefer, W. P., 168
 Schaeffer, R., 97, 120
 Scheidt, W. R., 159, 161
 Scherr, V. M., 112
 Scherrer, O. J., 132
 Schleyer, P. von R., 96
 Schmalfuss, S., 153
 Schmid, H-G., 130
 Schmidbaur, H., 190, 212
 Schmidpeter, K. H., 151
 Schmidt, H., 68
 Schmiedenknicht, K., 194

- Schmutz, J. L., 132
 Schofield, P., 9
 Scholer, F. R., 101
 Schram, E. P., 152, 174
 Schraml, J., 197
 Schrauzer, G. N., 157, 158
 Schrieke, R. R., 194
 Schrobilgen, G. J., 147
 Schrock, R. R., 180, 182, 196
 Schroeder, S., 196
 Schrymowycz, L. A., 178
 Schubert, V., 181
 Schug, K., 167
 Schultz, F. A., 158
 Schwab, G. M., 69
 Schwartz, J., 185, 196
 Schwendeman, R. H., 111
 Scoins, H. I., 10
 Scott, B. A., 141
 Searle, H. T., 132
 Self, K., 178
 Segre, U., 35, 43
 Seibert, W. E., 185
 Seider, P. G., 141
 Sellmann, D., 156, 157
 Selwood, P. W., 67
 Sengers, J. V., 13
 Senior, R. G., 155
 Senoff, C. V., 170
 Serafini, A., 112
 Sernin, G. K., 152
 Setaka, M., 34
 Sette, D., 14
 Seuftleber, F. C., 175
 Seyer, J. V., 130
 Seyferth, D., 187
 Shah, S. J., 87
 Sharavski, P. V., 68
 Sharp, D. W. A., 175, 186
 Sharp, G. J., 115, 151
 Sharstad, P. M., 194
 Shashidhar, R., 63
 Shaw, B. L., 100, 171, 197
 Shaw, R. A., 132
 Shchelokov, R. N., 183
 Shchembelov, G. A., 188
 Shchukarev, A. N., 68
 Sheahan, R. M., 170
 Shein, S. M., 70
 Sheldrick, G. M., 123
 Shen, Q., 126
 Shenav, H., 120
 Sheng, P., 32
 Shepherd, R. E., 166
 Sherwood, R. C., 153
 Shih, C. S., 34
 Shilov, A. E., 176
 Shimp, L. A., 180
 Shinra, K., 160
 Shirk, A. E., 115
 Shirk, J. S., 115
 Shive, L., 155
 Shive, L. W., 161
 Shomo, T., 160
 Shooter, D., 69
 Shore, S. G., 98
 Shriver, D. F., 111, 118
 Shteinman, A. A., 176
 Shu, P., 108
 Sigurdson, E., 183, 208
 Sillescu, H., 29
 Silver, B. L., 168
 Silver, J., 125
 Silvon, M. P., 179
 Simonneaux, G., 191
 Simpson, P., 135
 Simpson, S. K., 179
 Singh, A., 75
 Singh, B., 195
 Singhal, V. K., 56
 Singleton, E., 169
 Sinn, E., 173, 177
 Sinn, H., 196
 Skell, P. S., 179
 Skinner, H. A., 192
 Skowrónska, A., 135
 Sligar, S. G., 163
 Slutsky, J., 187
 Smart, L. E., 218
 Smith, I. W., 60
 Smith, J. D., 116, 194, 197
 Smith, J. S., 140
 Smith, L. R., 198, 218
 Smith, M. A. R., 175
 Smyrst, N., 145
 Snow, M. R., 166
 Snowden, B. S., 29
 Solarz, R., 77
 Solomon, E. I., 177
 Sommer, L. H., 188
 Sorrell, T. N., 164
 Spalding, T. R., 111
 Sparrow, G. J., 166
 Spencer, J. L., 106, 214, 218
 Spiesecke, J., 41
 Spiro, T. G., 150, 166, 168
 Springer, T., 41
 Spruijt, A. M. J., 54
 Squires, R. T., 37
 Stachnik, R. A., 115
 Stannislowski, A. G., 186
 Starks, D. F., 183
 Starowieyski, K. B., 195
 Stec, W. J., 135
 Steele, W. A., 25
 Steer, I. A., 110
 Stein, L., 145
 Steinfeld, J. I., 77
 Steinfink, H., 142
 Stelzer, O., 127
 Stephen, M. J., 32
 Stephens, F. S., 201
 Stevens, B., 86
 Stevens, J. R., 156
 Stiffen, W. L., 175
 Stilbs, P., 111
 Stillinger, F. H., 14
 Stobart, S. R., 120, 192
 Stoddart, J. F., 137
 Stofko, J. J. jun., 217
 Stohrer, M., 58
 Stoicheff, S. P., 25
 Stone, F. G. A., 105, 106, 186, 214, 216, 218
 Stone, K., 184
 Stonfer, R. C., 174
 Stopponi, P., 172
 Straley, J. P., 32, 35
 Stratton, C., 132
 Strauss, H. L., 13
 Streitwieser, A., 183
 Strekas, T. C., 168
 Strom, E. T., 29
 Strouse, C. E., 105, 106
 Strumolo, D., 205
 Stryta, B., 33
 Strzelecki, L., 37
 Stucky, G., 194
 Stults, B. R., 155, 160
 Su, L. S., 129
 Subramhayan, H. S., 33
 Sudot, T., 135
 Sugira, V., 178
 Sullivan, B. P., 99
 Sullivan, J. C., 170
 Summerford, J. W., 49
 Suna, A., 80, 88
 Sundberg, R. J., 166
 Suslick, K. S., 162
 Susuki, H., 158
 Symons, M. C. R., 127
 Tabashima, T., 158
 Tachikawa, H., 85, 86, 87
 Tachiyashiki, S., 118
 Takats, J., 149
 Tamaka, H., 178
 Tamas, J., 192
 Tameo, K., 187
 Tan, T.-S., 120
 Tanaka, J., 75
 Tanaka, M., 171
 Tang, S. C., 164, 170, 174
 Tang, S.-P. W., 166
 Tang Wong, K. L., 184
 Tanimoto, Y., 88
 Tano, K., 158
 Tarr, C. E., 58
 Tasset, E. L., 160
 Tatsumi, T., 159
 Taube, H., 154, 166
 Taupin, C., 37
 Taylor, B. F., 106
 Taylor, D., 170, 177
 Taylor, K. R., 152
 Taylor, L. T., 168
 Taylor, M. J., 92
 Taylor, N. J., 174
 Taylor, P., 147
 Taylor, R. C., 111
 Taylor, S. H., 215
 Tehan, F. J., 123

- Temme, F. P., 42
 Temperley, H. N. V., 6
 Templeton, J. L., 155
 Terinissi, P. A., 178
 Tewari, R. S., 190
 Thiele, K. H., 196, 197
 Thirase, G., 120
 Thomas, J. L., 184
 Thomas, K. M., 157, 171, 186
 Tietz, M., 153
 Timko, J. M., 138
 Timms, P. L., 105, 120, 179, 214
 Tirouflet, J., 150, 191
 Todd, L. J., 97
 Todd, S. M., 132
 Töpler, J., 41
 Tofield, B. C., 153
 Tokel-Takvoryan, N. E., 85
 Tokumaru, K., 88
 Tomchuk, E., 35
 Tomlinson, C. H., 179
 Torza, S., 55, 63
 Tossell, J. A., 114
 Towl, A. D. C., 203
 Tracey, A. S., 35
 Traylor, T. G., 162
 Treitel, I. M., 168
 Tretyakova, K. V., 152
 Tribo, M., 101
 Trigwell, K. R., 150
 Trotter, J., 132
 Troup, J. M., 155, 204
 Tsutsui, M., 183
 Tuck, D. G., 117
 Tucker, N. L., 197
 Tulinsky, A., 149
 Tundo, P., 138
 Tune, D., 206
 Turner, C. K., 206
 Turner, K., 180, 181
 Turner, L. A., 77
 Turner, R., 53
 Turney, T. W., 214
 Tweedale, A., 111
 Tyabin, M. B., 176
 Tyler, J. K., 130

 Uchida, Y., 159
 Ueda, F., 170
 Ugo, R., 176
 Ulmer, S. W., 194
 Unger, E., 127
 Upton, C. E. E., 212
 Ustynyuk, Yu. A., 188
 Uznánski, B., 135

 Vaira, M. D., 173
 Van Dam, E. M., 179
 Van der Wal, H. R., 184
 Vanderwielen, A. J., 119
 van Hove, L., 12
 Van Konynenburg, P., 25

 Van Oven, H. O., 184
 Van Tamelen, E. E., 156
 Van Vliet, P. I., 178
 Van Willigen, H., 75
 Vaughn, W. E., 17
 Vasapollo, G., 207
 Vasilev, G., 197
 Vdovin, V. M., 188
 Venanzi, L. M., 210
 Verkade, J. G., 127
 Verlet, L., 15
 Vickney, T. M., 158
 Vidal, M., 111
 Vieillard-Baron, J., 33
 Vilfan, M., 58
 Vincent, H., 123
 Vineyard, B. D., 171
 Virlet, J., 28
 Visintainer, J. J., 35
 Visser, J. P., 175
 Vitagliano, A., 178
 Voitlander, J., 69
 Volino, F., 46
 Vollmer, H. J., 196
 Volterra, V., 24
 von Schnering, H. G., 123
 Voronkov, M. G., 190
 Vos, A., 123
 Voss, J., 39
 Vrieze, K., 178
 Vyazankin, N. S., 183


 Waddington, T. C., 174
 Wade, K., 99, 126
 Wagner, B. O., 195
 Wagner, F., 173
 Wagner, R. I., 127
 Wainwright, T. E., 14, 16
 Waldvogel, G. G., 112
 Walker, F. A., 151
 Walker, J. M., 151
 Walker, M. L., 123
 Walker, R., 175, 183
 Wallbridge, M. G. H., 96
 Walser, R., 159
 Walton, D. R. M., 190, 197
 Walton, R. A., 151, 161
 Ward, I. M., 99
 Warner, L. G., 178
 Wasserman, E., 77
 Watanabe, J., 170
 Watanabe, S., 88
 Waters, J. H., 177
 Waters, T. N., 160, 178
 Watkiss, P. J., 125
 Webb, T. R., 154
 Webster, D. E., 176
 Wegner, P. P., 106
 Weiker, J. F., 165
 Weil, T. A., 210
 Weinkauff, J., 171
 Weir, J. R., 150
 Weiser, J. D., 97

 Weiss, E., 120, 195
 Weiss, K., 142, 181
 Weiss, R., 41
 Weisshaar, E., 68
 Welch, A. J., 106, 186, 216
 Welker, H., 68
 Weller, A., 86
 Wells, P. B., 176
 Wells, P. R., 119
 Werner, H., 206
 Weschler, C. J., 160, 163
 West, B. O., 170
 Westerhof, A., 184
 Westland, A. D., 152
 Westley, J. W., 140
 Weston, A. F., 112
 Weston, H. T., 63
 Westwood, N. P. C., 115
 Wetsel, G. C., 56
 Wharf, I., 118
 Wherland, S., 178
 White, A. H., 150
 White, A. J., 201
 White, C., 208
 White, W. I., 169
 Whiteley, R. N., 156, 180
 Whitesides, G. M., 185
 Whittingham, A. C., 94
 Whyman, R., 217
 Wiersma, R. J., 101
 Wigner, E. P., 69
 Wilcek, R. J., 187
 Wilkins, B. T., 127
 Wilkins, G. J., 126
 Wilkins, J. D., 149, 152
 Wilkinson, G., 183, 208, 209, 212
 Willet, R. D., 145
 Willey, G. R., 126
 Williams, C., 53
 Williams, C. E., 63
 Williams, F., 145
 Williamson, D. H., 209
 Williams-Smith, D. L., 179
 Wilmarth, W. K., 69
 Wilson, R. D., 127, 145
 Windhorst, K. A., 171
 Winkler, E., 181
 Wittel, K., 115
 Wölfel, W., 58
 Woessner, D. E., 29
 Wojtowicz, P. J., 32
 Wolf, A. D., 187
 Wolf, L. K., 179
 Wolfbeis, O., 179
 Wolfgang, R., 190
 Wong, C. S., 210
 Wong, C. W., 210
 Wong, Y. S., 214
 Wood, R. H., 115
 Wood, W. W., 14
 Woods, M., 170
 Woods, M., 132
 Woodward, M. R., 56

- | | | |
|-------------------------------------|-----------------------|-------------------------|
| Woodward, P., 175, 206, 215, 216 | Yamaoka, S., 142 | Zana, R., 47 |
| Wozniak, W. T., 150 | Yarno, T., 160 | Zanella, A. W., 171 |
| Wreford, S. S., 150 | Yee, S., 159 | Zannoni, C., 34, 35, 44 |
| Wrighton, M. S., 155, 196, 199 | Yo, F. Y., 105 | Zarella, A. W., 167 |
| Wulf, A., 40 | Young, D., 179 | Zavizion, Y. S., 195 |
| Wurrey, C. J., 129 | Young, G. B., 211 | Zav'yalov, V-I., 188 |
| Wyllie, G., 18 | Younger, D., 174 | Zeldin, M., 124, 190 |
| Wyrsh, D., 86 | Yun, C. K., 40 | Zernike, F., 10 |
| | | Zimmer, L. C., 178 |
| Yakel, H. L., 113 | Zachariasse, K., 86 | Zintl, E., 123 |
| Yamamoto, A., 196 | Zack, N. R., 174 | Žumur, S., 40 |
| Yamamoto, Y., 190 | Zakharkin, L. I., 195 | Zupančič, I., 40, 41 |
| | Zakharov, P. I., 188 | Zwanzig, R., 9, 16 |

+1 50 2/25/77
MAR 10 '77
172 See A

BROOKLYN PUBLIC LIBRARY



3 4444 03183 9251

1517



The Chemical Society

Specialist Periodical Reports

The following titles in the series are currently available

Photochemistry
Mass Spectrometry
Carbohydrate Chemistry
Amino-acids, Peptides, and Proteins
The Alkaloids
Terpenoids and Steroids
Organophosphorus Chemistry
Organic Compounds of Sulphur, Selenium, and Tellurium
Foreign Compound Metabolism in Mammals
Aliphatic Chemistry
Alicyclic Chemistry
Saturated Heterocyclic Chemistry
Aromatic and Heteroaromatic Chemistry
Environmental Chemistry
Biosynthesis
Fluorocarbon and Related Chemistry
Organometallic Chemistry
Inorganic Chemistry of the Transition Elements
Inorganic Chemistry of the Main Group Elements
Inorganic Reaction Mechanisms
Radiochemistry
Spectroscopic Properties of Inorganic and Organometallic Compounds
Electronic Structure and Magnetism of Inorganic Compounds
Molecular Spectroscopy
Nuclear Magnetic Resonance
Electron Spin Resonance
Surface and Defect Properties of Solids
Statistical Mechanics
Reaction Kinetics
Dielectric and Related Molecular Processes
Electrochemistry
Molecular Structure by Diffraction Methods
Colloid Science
Chemical Thermodynamics
Theoretical Chemistry

Further information about any of these publications can be obtained from: The Marketing Officer,
The Chemical Society, Burlington House, London W1V 0BN.